Self-Healing Polymer Matrix Composite Matrix Materials Using Hindered Urea Bonding

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Self-Healing Polymer Matrix Composite
Matrix Materials Using Hindered Urea Bonding

By

Joseph F. Schevtchuk

A Thesis Submitted in Partial Fulfillment of the requirements for the Degree of
Master of Science in Manufacturing and Mechanical Systems Integration

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Nomenclature:

**BST**: Bag Sealant Tape  
**CH₃**: Methyl group  
**FTIR**: Fourier-transform infrared spectroscopy  
**DBTDA**: Dibutyltin diacetate  
**DSC**: Differential Scanning Calorimetry  
**DMF**: Dimethylformamide  
**Dogbones**: Cast polymer tensile testing specimens  
**HMDI**: Hexamethylene Diisocyanate, aliphatic diisocyanate.  
**HUB**: Hindered Urea Bond  
**RBF**: Round Bottom Flask  
**T₉**: Glass Transition Temperature  
**TBEU**: N, N’-Bis (tert-butyl) ethylene diamine (1, 2-Bis (tert-butyl amino) ethane)  
**TDI**: Toluene Diisocyanate  
**TEA**: Triethanolamine  
**TEG**: Triethylene Glycol  
**XDI**: m-Xylene diisocyanate, aromatic diisocyanate.  
**XDI-0**: Polymer derived from fully aliphatic diisocyanate (HMDI) based pre-polymer.  
**XDI-25**: Polymer derived from mixed aromatic (25%, XDI) and aliphatic (75%, HMDI) diisocyanate based pre-polymer.  
**XDI-50**: Polymer derived from mixed aromatic (50%, XDI) and aliphatic (50%, HMDI) diisocyanate based pre-polymer.  
**XDI-75**: Polymer derived from mixed aromatic (75%, XDI) and aliphatic (50%, HMDI) diisocyanate based pre-polymer.  
**PMC**: Polymer Matrix Composite  
**KF**: Karl Fisher Titration  
**KKAT-6212**: Urethane catalyst, zirconium chelate dissolved in reactive diluent.  
**NCO**: Isocyanate group  
**OH**: Hydroxyl group  
**MW**: Molecular Weight  
**NH₂**: Amine group
Committee Approval

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Abstract:
Polymer matrix composites (PMCs) utilize thermoset resins in large part because of their low starting molecular weights which allow for good reinforcement infiltration prior to curing. Formed networks owe much of their mechanical properties to covalent crosslinks tethering molecules within the matrix. Traditional covalent bonds are irreversible and thus damaged composites are either repaired or replaced. For the former, traditional repair techniques remain costly and time consuming. Dynamic covalent bonds represent a potential alternative to traditional covalent bonds. These unique chemical groups can be tailored to engender thermoset-like characteristics at use-temperatures and thermoplastic-like behavior at elevated temperatures thus enabling self-healing. In this work a thermally mendable self-healing PMC matrix material is proposed enabled by the use of hindered urea bonds. In this investigation traditional crosslinked networks containing hindered urea bonds (HUBs) with varying levels of aromatic content have been synthesized. Optimization of synthetic processes presented in this research has allowed for the formation of materials with varied material properties such as $T_g$, toughness and tensile strength. These polymers have been used to investigate the restoration of mechanical properties when exposed to thermal stimulus promoting accelerated self-healing. It is envisioned that advanced polymeric matrix materials have numerous practical applications including but not limited to composite structures and military vehicles alongside commercial applications as self-healing polymers.
CHAPTER 1: Overview

1.1: Introduction:
Polymer Matrix Composites (PMCs) are composites which consist of a polymer matrix, typically a thermoset resin, which are then strengthened with a fiber reinforcement. Carbon fiber is the most prevalent reinforcement material used in the aerospace industry. Other reinforcement systems are used such as fiberglass and Kevlar are also being used at an increasing rate due to their widespread application basis in aerospace, commercial sporting goods, and other industries. PMC laminates are primary utilized for their desirable specific strengths and specific stiffness.

Thermoset resins are typically used as matrix materials for composite applications due to their compatibility with fiber reinforcements, their strength, chemical resistance, and ease of composite wet-out during the layup process. The strength of thermoset resins comes from the covalent bonds allowing for a fully crosslinked network to be formed. These covalent bonds have superior bond strength when compared to secondary bonds such as hydrogen and Van Der Waals bonds which are present in thermoplastics. The irreversibility of thermoset (crosslinked) networks which gives them their superior strength also means that these polymers when used as a fiber reinforced composite as a matrix material cannot be repaired or reprocessed by traditional methods.

Due to the inability to repair thermoset polymers considerable interest has been placed in developing advanced matrix materials with self-healing characteristics. In this study the design of an intrinsically self-healing polymer matrix material will be researched in order to provide a mendable advanced matrix material for composite applications. Applications of the proposed PMC matrix material are not limited to aerospace, as automotive, energy, and recreation sectors stand to benefit by the implementation of these polymers.
1.2: Potential Applications of Polymer

Initial development of the polymer focused on the increase in $T_g$ and subsequent stiffness of the polymer to allow for structural application with aerospace structures of primary interest. However this chemistry allows for a high degree of modification through the alteration of aromatic content allowing for this polymer to be potentially developed for an array of potential applications. The following section will outline potential applications of interest that this polymer chemistry may be suited for.

1.2.1 Damage Tolerant Composite Matrix Materials

PMC laminates when subject to out-of-plane loading scenarios, in particular impact may experience localized delamination resulting in a decreased load carrying capacity. Localized delamination at a non-visible level where the damage is considered to be not observable via inspection, or “Non-Visible Impact Damage” however has been found negligible (NASA 19920023283, 1992). These initial matrix cracking sites however negligibly small are found to lead to crack propagation, delamination, and eventual decreased load carrying capacity of the composite structural member.

Once PMC laminate localized failures are observable they may be classified into categories which can be used to determine life limiting, or load enhancement factors (LEF) that help determine knock-downs in service life capabilities. These LEFs are based on the assumption that sub-critical matrix failures from impact events lead to failure initiation and fatigue based propagation that will lead to laminate level failures that may be catastrophic in nature (Seneviratne, Tomblin 2010).

As sub-critical matrix failures are often life-limiting due to their inevitable crank propagation and subsequent laminate level failure, much interest has been placed in the ability to reduce sub-
critical matrix crack propagation through the development of PMCs capable of arresting crack propagation. Examples of sub-critical matrix-failures of a thermoset matrix are presented below as reference allowing us to introduce the concepts of Intralaminar cracking (within the lamina, or ply) and Interlaminar cracking (between laminas or plies).

Figure 1: Laminate Sub-Critical Matrix failure Types

These sub-critical matrix failure sites represent non-visible impact damage and therefore fall below the inspection threshold making these damages unknown and therefore unclassifiable to allow for proper LEF considerations to be applied. As it has been found that these non-visible damage sites are structurally negligible (NASA 19920023283, 1992) until inevitable crack propagation allows for newly formed barely visible impact damage (BVID) or visible impact damage (VID) to be found and classified for LEF analysis. For clarification of VID, VBID, and other localized damage site types figure 2 is available for reference.
Type 1 impact damage represents the start of the visible inspection threshold (Strong, 2008) which allows for observation and correction of damaged laminates. It is envisioned that matrix self-healing strategies such as those proposed in this research would be most appropriate for early undetectable or barely detectable damage inclusive of types 1-3.

With the problem of identified damage to a structural composite laminate using traditional thermoset matrix materials one is presented with a fix, life limit, or replace decision however methodologies for fixing composites are limited as covered in 1.4, Literature Review.

Self-healing PMC matrix materials present an opportunity to potentially self-heal sub-critical matrix cracks before they propagate into classifiable BVID/VID damage types... Alternatively once inspection threshold has been reached the potential for accelerated self-healing through thermal stimulation becomes an option.

It is hypothesized that thermally accelerated self-healing may allow for the development of PMC matrix materials that will allow for increased damage tolerance and fatigue life in structural PMC laminates.
1.2.2 Ballistic Resilience
Due to the low glass transition temperatures of several of the polymers investigated in this research, applications for the polymer as a matrix in load bearing structural composite members may be limited by the low modulus of the polymers. However it is envisioned that these polymers may be useful as matrix materials in ballistics applications where low $T_g$ matrix materials are acceptable as they may act as elastomeric flexible matrix materials allowing for energy absorption.

The self-healing properties of the polymers investigated in this research primarily as a matrix material capable of healing sub-critical inter and intra laminar matrix failure are also proposed as having the potential of acting as viable matrix materials for the creation of composite materials designed for applications in which ballistic resilience is of value. As Kevlar’s ability of load transfer and energy dissipation is based on the transfer of shear through a fibril network (McAllister et. al, 2013). It is hypothesized that an elastomeric low $T_g$ PMC matrix material could allow for fibril formation and subsequent ballistic resilience.

1.2.3 Self-sealing & re-sealable packaging
Through observation of placing low $T_g$ ($T_g = \sim 5^\circ C$) polymer specimens in vials for storage it was found that the specimens meld together when kept in intimate contact. Through this observation it is found that these polymers not only heal but also exhibit reversible or temporary adhesive bonding capabilities. Due to this capability this polymer system has potential in packaging applications where mating surfaces can be peeled apart and placed into intimate contact and thus re-sealed through the (re)formation of HUBs. This self-sealing packaging technology application could be used at room temperature or allow for rapid sealing of packaging with the application of heat.
1.2.4 Urethane Paints & Protective Coatings additive:

As this polymer is a hindered urea its chemical compatibility lends itself to its introduction as an additive in existing urethane chemistries. It is hypothesized that the introduction of HUB bearing polymers as a paint or coating additive could allow for scratched or damaged coatings to self-heal. This however requires that the polymers remain in intimate contact to self-heal retaining a protective barrier layer despite damage through minor punctures or abrasions in which bulk material is not removed.

1.2.5 Consumer Electronics Protective Coatings:

Current consumer electronic devices such as smart phones, tablets, and laptops often rely on screen protectors. Screen protectors are often the first line of defense against abrasions and cuts acting as a protective film. Given the ability to produce these self-healing polymers as a thin transparent film it is feasible to propose these polymers as a material choice these protective coating applications. With polymers whose \( T_g \)'s are below room temperature scratches on these polymers will be allowed sufficient chain mobility to self-heal restoring the transparent quality in an undamaged screen protector while restoring the protective film. Particular interest is placed on smart-phone screens due to their typical storage in the consumer’s pocket; this common storage space allows for radiant body heal to raise the temperature of the polymer protective coating thus enabling an accelerated self-healing process.

1.2.6 Self-healing Automotive Tire Inner Liner Material:

The use of self-healing polymers as an inner liner material is possible as the application of a thin layer self-healing, self-sealing material with a sub-ambient \( T_g \) would allow for a tire liner that could resist leaking as minor punctures could be healed through the formation of HUBs at ambient temperatures.
1.3: Background & Review of Prior Work
The development of a polyurea based self-healing polymer demonstrating the ability to self-heal through the action of dynamic covalent bonds or more specifically hindered urea bond has been a recent addition to the field of self-healing polymer chemistry (Ying, et al., 2014).

Hindered urea bonds (HUBs) are hypothesized to become dis-associated under stress and re-associate when put back into intimate contact after the mechanical failure of the polymer specimen. The self-healing polymer created however has a glass transition temperature (Tg) which is well below room temperature resulting in an elastomeric material with low strength and stiffness. The chemistry used in this original study was based on a purely aliphatic chain structure explaining the low Tg observed. This enhanced chain mobility within the polymer coupled with a properly tuned bond allows for self-healing at room temperature.

A polymer which acts as a stable solid or elastomer as opposed to an elastomeric gel is desirable for material applications therefore interest lies in making a stiffer, higher Tg polymer than previously produced. The utilization of a HUB based polymer relies on the polymers affinity towards the association of the HUB as opposed to the disassociation which is known as $K_{eq}$, the equilibrium constant which is the ratio of $K_1/k_{-1}$ where $K_1$ is the association rate of the HUB and $k_{-1}$ is the disassociation rate of the HUBs which these polymers are based off of. Therefore in order to maintain this affinity for self-healing through preferential association a high $K_{eq}$ must be present. These desirable HUBs are formed when TBEU and HMDI are reacted resulting in $K_{eq} = 7.9 \times 10^5$, $k_{-1} = 0.021$ as found by Ying & Cheng in 2014 through nuclear magnetic resonance (NMR) spectroscopy studies. These same studies also pointed towards a similar disassociation rate of HUBs formed from the reaction of TBEU and XDI resulting in $K_{eq} = 7.1 \times 10^4$, $k_{-1} = 0.019$ (Ying & Cheng, 2014). Due to the similarities in $k_{-1}$ for both aromatic and aliphatic isocyanates it follows that one may interchangeably use HMDI and XDI in the
formation of similar HUBs thus leading towards the development of hybridized polymers contain both aromatic and aliphatic isocyanates (Bruce, Lewis, 2017).

Further research on this polyurea chemistry by Bruce and Lewis (2017) demonstrated that aromatic networks bearing HUB also exhibited the ability to self-heal. In their work it was shown that increasing aromatic diisocyanate concentration increased $T_g$ thereby creating a stronger and stiffer polymer. With the increased $T_g$ the polymer must be exposed to thermal stimulus to allow for mobility within the crosslinked network for self-healing to occur. Constant healing conditions of polymers with higher concentrations of aromatic content however have exhibited a reduced efficacy of towards self-healing when compared to polymers with lower aromatic content.

1.4: Literature Review
The following section outlines technologies relevant to this research and examines prior work in similar fields that contributed to the conceptual development of this research.

1.4.1 Current Self-Healing Polymer Technology
*Extrinsic Self-Healing*
Extrinsic self-healing is a term used for polymers that contain non-homogenous additives that are dispersed within the polymer which enables repair of the polymer architecture. One method of extrinsic self-healing was demonstrated by the addition of a microencapsulated liquid healing agent and a catalyst to a polymer matrix. When fracture occurs the microcapsules are broken thus allowing the two ingredients to mix and cure resulting in local repair (Kessler, Sottos, & White 2003). Another method of extrinsic self-healing demonstrated used a vascular network of hollow glass fibers containing healing agents and catalysts which when fractured promote local healing (Blaszik et al. 2010). Liquid healing agent/catalyst systems are however limited as they
are only able to heal once per localized damage site as activation requires mechanical stimulus to break open a finite amount of contained healing agent.

The addition of thermoplastics additives within the polymer network allows for the remelting of these additives to allow for flow and mechanical bonding within a damaged polymer. This repair technique when used in epoxy resin systems has demonstrated repair efficiencies up to 65% at the first healing cycle. However diminishing healing efficiency was observed with secondary repair cycles. (Hayes et al. 2007)

**Intrinsic Self-Healing**

Intrinsic self-healing polymers allow for a self-contained healing polymer architecture which is capable of being triggered by external stimulus such as heat. The advantage of intrinsic self-healing polymers is that these polymers could theoretically perform an indefinite number of healing cycles as opposed to the limited number of healing cycles allowed by extrinsic self-healing techniques.

Self-healing polymer development for structural composites applications as is the focus of this research is centered on crosslinked thermoset networks due to their processing and mechanical characteristics. Early development of reversible bonding is credited to the work of Diels and Alder in 1928 which discovered the ability to form thermally reversible covalent bonds through cycloaddition (Murphy, Wudl, 2009). Subsequent work on the topic of thermally reversible covalent bonds using Diels Alder chemistry was later conducted resulting in the creation of thermally mendable crosslinked polymers (Chen et al., 2002).

Dynamic covalent bonds were discovered in polyurea chemistry through the advent of Hindered Urea Bond (HUB) reactions. These HUB require an isocyanate and an amine to create a urea
bond which can reversibly disassociate. (Ying et al., 2014). Figure 3 shows the formation and disassociation of a HUB bond:

![HUB bond diagram](image)

**Figure 3:** HUB association and dissociation providing self-healing capability.

The reaction of diisocyanates and amines to create ureas or polyureas is common for the production of polyureas. However the reaction used by Ying and coworkers using an amine containing a bulky nitrogen substituent group (represented by the grey circle in figure 3) can be used to tune the strength and reversibility of the HUB.

Ying et al.’s research focused on the creation of a polymer that would heal at slightly elevated temperatures (37°C). To achieve satisfactory properties required that the reaction favored HUB formation where the equilibrium constant ($K_{eq}$) was found to be $\sim 10^5$. However, to achieve self-healing required a measurable disassociation rate ($k_1$) at healing conditions.

It is suspected that self-healing is a temperature dependent phenomena requiring both high chain mobility and favorable reaction kinetics. While Ying et al.’s work demonstrated the capability to self-heal at low temperatures their low $T_g$ polymer has too low of a modulus and strength to be considered for structural applications. Prior research found that self-healing efficiencies appeared to increase when thermally treated as opposed to at room temperature while treatment time also appeared to have a significant effect of healing efficiency (Ying, et. al, 2014). Polymers of low...
$T_g$ are thought to allow for a greater understanding of self-healing characteristics of HUBs while they remain unfit for structural applications.

Recent research by Bruce & Lewis in 2017 has shown that mechanical and thermal behavior of the polymers could be altered by increasing the aromatic content of the polymer networks. Continued research is focused on development of a self-healing polymer which would have mechanical properties allowing for the use of the polymer in structural applications. By increasing aromatic content the polymers lose chain mobility and subsequently the ability to self-heal at room temperature but required elevated temperatures to allow for self-healing to occur.

1.4.2 Failure Mechanics of Composites in Aircraft

As this research was intended to develop a self-healing or thermally mendable matrix material for use in fiber reinforced composites it is crucial that the reader has an understanding of the failure mechanics of composites.

*Impact Damage*

Impact damage to composite structures is of crucial concern as a superficial impact caused by FOD (Foreign Object Debris) can become the source of a crack propagation within a composite laminate. In turn, this can lead to delamination which severely reduces the strength of a composite component. Impact damage in composite laminates can also enable moisture intrusion into the cracks within the laminate and this further opens cracks through freeze/thaw cycling. Matrix damage severely compromises the ability to transfer loads throughout the fibrous reinforcement material resulting in loading scenarios within a laminate which can lead to further laminate damage as discussed next under “Delamination”.
Delamination

Delamination (Interlaminar Matrix Failure) within a composite laminate has been shown to reduce strength in tensile loading due to the isolation of sub-plies within the laminate which are unable to fully support loading scenario (DOD, 2002). Concerns with the isolation of plies due to delamination include the loading of off-axis plies in tension which are not balanced or symmetrical while isolated. Plies which are crucial for load transfer within the laminate which become isolated from the rest of the laminate as they no longer share the same interlaminar bonding through a continuous polymer matrix due to partial delamination will experience less strain than the intact fully laminated plies which are subject to loading. This scenario leads to the development of a shear plane in which delamination can further propagate. The plies which are experiencing greater strain may eventually experience fiber failure and catastrophic laminate failure. Edge delamination is a major concern as delamination can propagate along the edge of a laminate. Impact damage can be responsible for matrix damage and subsequent delamination which can propagate user stress without edge conditions present. In compression, delamination as a result of matrix failure from impact can reduce the strength of a laminate resulting in the buckling of a composite part far below the design load limit.

Fatigue

Fatigue within a composite laminate can lead to failure through multiple mechanisms due to the nature of a non-isotropic material. Due to this combined with the wide range of composite laminate stacking sequences that can be used each laminate will have unique fatigue characteristics. In order to understand the nature of fatigue in composites probabilistic numerical models have been developed from data scatter from extensive composites fatigue testing in order to provide estimates of fatigue characteristics of laminates in which experimental data is
This allows for the design of fatigue testing experiments using LEF (Load Enhancement Factor) techniques resulting the reduced testing time on a laminate specimen though increased loading at reduced number of loading cycles. Currently analysis approaches for modeling fatigue in composite aerostructure are required to demonstrate their reliability through comparison to test data using full scale test articles in order to attain FAA certification (DOT/FAA/AR-10/6, 2011). The practice of requiring full scale fatigue test specimens is expensive and time consuming however this practice will remain critical until numerical methods have proven reliable.

Aeroelastic Considerations

The stiffness of an aerostructure is a primary consideration in the design of flight surfaces as the aeroelastic properties of a flight surface dictate the ability of the flight surface to damp oscillations within the structure. Due to this matrix damage is a major concern with respect to structural composites in aerospace applications as the decreased stiffness of a laminate due to matrix damage causes an increase in the magnitude of aeroelastic oscillations (Strganac T.W., Kim, Y.I, 1996). This increase in the amplitude of the oscillations in the event of flutter is a concern as it is a potential cause of further vibrational damage to the aerostructure. The flutter characteristics of a flight surface are dictated by three factors: Inertial, Aerodynamic, and Elastic forces. The concern with the current techniques of composite repair is that repairs to composite structures using current techniques can alter the mass distribution within a wing or aerostructure as patching, and scarfing processes are material removal and addition processes. Composite repair processes will also alter the stiffness of a wing resulting in changed elastic properties when attempting to repair a loss of stiffness due to matrix failure.
1.4.3 Composite Repair Techniques

Scarfing

The most common composite repair technique used in the aerospace industry is scarfing. Scarfing is a process in which damaged composite material is physically removed through either diamond machining or grinding processes and patching the damaged cite using an adhesive bonded metallic or composite scarf patch. A doubler can then be applied over the scarfed area which acts to improve aerodynamics and aesthetics of the scarfed and filled composite component. This repair process is time intensive and requires that the part which has been scarfed can still handle the design load before the application of the scarf; this implies that the scarfing process does not allow for repair of critically damaged parts on commercial aircraft. The DOT and FAA do not allow for scarfing to serve as a structural repair as quality of the adhesive bonding between the scarfed surface and repair patch is difficult to measure and therefore cannot be relied upon for loading scenarios as it is assumed that the scarfed area is not properly bonded as it cannot be verified using currently available non-destructive testing methodologies (Wang, Duong, 2016).

Patching

Patching is a method of damaged composite repair in which the area of damage is physically removed in the same fashion in which a laminate is scarfed. However with patching a scarf repair patch is not used, instead the void is filled completely with an adhesive and a patch material is laid over the adhesive filler much in the same way body filler is used in automotive applications.

Patching has shown promising results for the restoration of compressive strength of composites (Park, Kong, 2011). However in compressive loading scenarios the majority of a composites
strength comes from the matrix so it follows that the placement of a filler material (adhesive) can be used to transfer compressive loads throughout a specimen. In tensile loading scenarios patching however as the filled and patched area may function as a major stress concentration as there is a lack of reinforcement to transfer loading.

**Bolted Repairs**

Bolted repairs are repairs to composite laminates in which a patch is directly through bolted onto the surface of the composite part. This techniques is used as “battle patching” due to its fast turnaround time. Like the name implies this technique was developed as a way to reduce repair times for combat aircraft. Bolted repairs in composite aerostructures are a temporary solution to impact or battle damage which can be quickly affixed to an airframe, however bolted repairs are not final fix to the composite airframe as they have adverse effects on radar cross section and weight distribution of the aircraft. (Hughes, 1990)

1.4.4 Composite Inspection Techniques

**Visual**

The primary technique for a first round inspection of composite structures is visual as composite impact damage is classified in two primary groups as follows:

1. VID: Visible Impact Damage
2. BVID: Barely Visible Impact Damage

The problem however with visual inspection of a composite laminate is that the visible portion of an impact sight is the “tip of the iceberg” in that only a small portion of the damage is visible to even a trained eye. Impact damage in a laminate may be difficult to notice due to their small size in relation to the larger area of damage beneath however the majority of damage due to an
impact is experienced by the matrix resulting in subsequent cracking and delamination of the composite structure.

**Thermographic**

Thermographic analysis can be performed on composite laminates in order to determine the extent of below the surface impact damage through the rapid localized heating of a damaged area followed by thermographic imaging of the area. This technique is called Pulse Phased Thermography. This works as the subsurface defects disturb the heat flow through the composite and are then recognizable as areas of interest through evaluation of thermographic imagery (Maier et al. 2014).

**Ultrasound**

Ultrasonic testing (UT) of composite laminates is commonplace in the aerospace industry as it allows for the visualization of defects with a composite laminate such as delamination sites and interlaminar cracks. The operating principal is that the material being scanned should be semi-homogenous so that sound should travel through the intact composite at a uniform rate. Cracks and defects cause a shift in the rate of received response to the receiver thereby allowing for their detection. The advantage of UT is that it allows for the locating and mapping of non-visible subsurface defects and can be done on parts with complex geometries.
CHAPTER 2: Purpose of Research

2.1: Problem Statement
As advanced composites use thermoset matrix materials damage to these laminates cannot be easily repaired. Current composite repair techniques are expensive and do not allow for the recovery of the composite parts mechanical properties and induces stress concentrations within the laminate. Research in self-healing polymers is meant to allow for development of a PMC matrix material allowing for the efficient repair of matrix cracking in damaged PMC laminates.

2.2: Hypotheses
The overarching hypothesis is that a polyurea based self-healing polymer has the potential to act as a PMC matrix material. This would allow for thermal mending of damaged composite components. Through the modification of current intrinsic self-healing polymers presented by Ying et al, 2014 and Bruce & Lewis, 2017 a polymer could be developed which would be a functional matrix material for usage in structural composites applications. In order to progress toward the goal of the effective rational design of polymers allowing for the repair of composite laminates utilizing self-healing PMC matrix materials it is required that the healing efficiency and healing conditions and effects are understood through the testing of several hypothesis.

H₁: The thermoset HUB based polymer will demonstrate the capability to self-heal when placed into intimate contact with itself, thus simulating the healing of intralaminar and interlaminar matrix cracking at a macro scale allowing for the evaluation of healing efficiencies of the neat resin.

In order to allow for the future development and testing of the HUB based PMC matrix material primary focus has been places on the development of the neat resin as it is a prerequisite to PMC laminate development. To test the potential of the application of this material as a self-healing PMC
matrix material the neat resin must first be tested to evaluate its healing efficiency as a constituent of future laminate development. Testing of this hypothesis is intended to allow for confirmation and comparison of similar polymer development work undertaken Lewis & Bruce in 2017.

H2: Temperature has a significant effect on healing efficiency of the HUB based polymer as a function of healing efficiency and the departure of ambient conditions from the $T_g$ of the polymer as $(T-T_g)$.

As the use of Self-Healing PMC matrix materials is proposed in this study as a novel approach for the repair and of fiber reinforced PMC laminates an understanding of the ability to accelerate the self-healing process through the application of heat is critical.

H3: The thermoset polymer containing HUBs can be manufactured using available synthetic technologies to produce a neat resin that can be used with common composite manufacturing techniques allowing for the successful production of a fiber reinforced PMC laminate.

As this research involves the synthesis of advanced polymeric materials it is crucial to demonstrate a technology maturation rendering the polymer system closer to commercial viability. The requirements of fulfilling $H_1$ are as follows:

1. HUB based polymers can be produced without critical defects.
2. The manufacture of HUB based polymers specimens can be used to allow for mechanical evaluation of these polymers.
3. HUB based polymers must be stable in mechanical properties without issues such as solvent entrapment.
4. HUB based polymeric matrix material must be capable of wet-out of fiber reinforced PMC laminate using traditional vacuum bagging techniques without the assistance of specialized manufacturing methods.
2.3: Significance of Research
As previous work (Ying, et. al, 2014), (Bruce, Lewis, 2017) has demonstrated the feasibility of the creation of a thermally mendable thermoset polymer. This work leads towards the usage of the polymer in a composites matrix application. If the chemistry present can be modified to allow for usage in composites applications it is possible that self-healing composite matrix materials could allow for advanced repair techniques of damaged composite components. Research in a self-healing PMC matrix material may lead to advancements in composite aerostructure repair allowing for both civil and military aircraft operators to quickly repair damaged aircraft. Fast repair time for aircraft is a crucial requirement to airline operators who stand to lose up to $100,000 USD per day per plane for AOG (aircraft on ground) time (Wood, 2008).

With the primary focus on the development of structural PMC matrix materials through the development of a self-healing polymer architecture there is significance in the potential applications of the polymers developed in this research as outlined in 1.2, Potential Applications of Polymer.

2.4: Experimental Design
The focus of this experimentation has been the validation of the concept of self-healing PMC matrix materials. Before the ability to evaluate the polymer as a matrix material the polymers bulk material properties had to be evaluated in terms of its ability to self-heal as considered in H1. Testing of H1 requires the casting of high quality polymer specimens into tensile testing coupons, or “dogbones”. In order to remain consistent with prior work (Ying et. al, 2014), (Bruce, Lewis, 2017) the dogbone geometry shown in figure 4 has been utilized.
The geometry utilized allows for a small volume (.500cc) of polymer to be used in order to maintain small polymer synthesis volumes: with a single batch synthesis able to produce between five and seven dogbones. Variance in quantity of dogbones manufactured from constant volume of polymer arises from the amount of polymer which is lost in as transfer losses during transfer from the reaction vessel. Another source of variability was the manual casting operation in which manual dexterity is required to pour small amounts of a viscous liquid in precise increments in rapid succession.

A pre-requisite to experimental design was a polymer development effort to allow for the repeatable, consistent manufacture of high quality tensile testing specimens. This involved dozens of experimental syntheses. Many of these experimental syntheses were exercises in root cause identification as the large quantity of factors involved in the synthesis of the polymer coupled with the time intensive nature of each batch produced made attaining reproducible polymer batches difficult before a systematic top-down procedure was developed. For details on the polymer development process see Chapter 3: Synthesis of Polymer.
Tensile testing of the polymer dogbone specimens was performed using an Instron 5500 series dual column tensile load frame using a 1KN load cell fitted with pneumatic jaws. Testing was performed using 2 inches/minute crosshead travel rate with an initial gauge length of 0.300”.

Preliminary testing of several specimens found the low T<sub>g</sub> polymer specimens to behave as elastomers resulting in unpredictable failure sites resulting in failures at the jaws and outside of the gauge area.

These issues with testing the polymers of the given geometry was a new phenomenon as it pointed towards the successful synthesis of polymers with much greater toughness, stress at failure and elongation at break. Prior work had never experienced these issues presumably as they were solvent loaded (Bruce, Lewis, 2017) and acted more as elastomeric gels as opposed to elastomeric polyurethanes.

Due to this dogbone notching in order to create a controlled stress concentration was performed in order to maintain a consistent failure site for the polymer tensile specimen. A simple fixture was 3-D printed to allow for consistent notching be performed manually using a razor blade as shown in the following figure.

Figure 5: Specimen Notching Rig
Figure 6: Specimen Notch & Gauge Length Dimensions

Dimensions for the notch were chosen to create a notch with a small yet visible feature with a controlled amount of area reduction from the cross section (10% area reduction). The 60 degree notch was chosen to ensure that a removal of material would not allow for intimate contact to become reestablished that would change the healing interface area.

To check on the consistency of notched specimens and ensure failure was occurring at the notch site quality checks using a microscope at 75x magnification was performed with the following results:

Figure 7: Notched Specimen, Prior to Testing (XDI-25 specimen shown).
A source of experimental variance is attributed to the manual notching of tensile testing specimens as slight “overcutting” occurred. This overcutting lead to a greater reduction in cross sectional area intact as intended which is attributed to variance as the notch, cut at a 60 degree angle was intended to ensure that the two faces creating the notch would not be allowed to return to intimate contact. By overcutting the samples a smaller gauge area than designed would be tested as tensile testing occurred immediately after notching. This would then follow that the initial tensile strength of the specimen is lower than accounted for with the measurements of cross sectional area. Variance in XDI-25 results resulting in healing efficiencies above 100% is through to be due to this overcutting issue as the specimen was able to heal over the overcut area resulting in a larger cross sectional area than the initial testing resulting in healing efficiencies that would otherwise not be possible as 100% healing efficiency is the maximum without explainable variance contributing to results beyond this. This is one major disadvantage of notching the specimens as it introduces this variance thus adding emphasis towards arguments in favor of a revised specimen geometry.

Figure 8: Notched Specimen, Post Tensile Testing (XDI-25 specimen shown).
Tensile testing of the notched specimen was shown to allow for controlled failure of the polymer. One part of the experimental setup of note is the usage of 1” binder clips to assist in providing clamping force to the pneumatic jaws. This was found necessary as preliminary testing found that the jaws did not provide sufficient clamping force resulting in the specimens slipping during testing. The inability to break these new, tougher samples is reflective of the synthesis improvements discussed later in this thesis.

![Figure 9: Tensile Testing Methodology](image)

Figure 9 represents a time series showing typical fracture of an HUB containing polymer. Note that clips in addition to pneumatic jaws were required to prevent jaw slippage. Tensile testing was performed in the RIT APC lab at an average temperature of 23°C and an average relative humidity of 22% in April 2018.

In order to test H2 which states that temperature has a significant effect on healing efficiency the following experimental design was organized:

Polymers investigated in this experimental design consist of a fully aliphatic polymer with no XDI which is referred to as XDI-0, a polymer which has 25% aromatic NCO content through the addition of XDI which is referred to as XDI-25, and a polymer containing 75% aromatic content through the addition to XDI which is referred to as XDI-75. XDI-0, XDI-25, and XDI-75 were all post cured for 24 hours at 60°C sharing the same treatment prior to initial tensile testing as a post-curing operation.
Each batch resulted in the formation of between seven and eleven test specimens within the batches. These were randomized and sub-three groupings of equal two-three specimens of similar quality were segregated. Grouped specimens were given alphabetical IDs signifying batch & letter (Batch 99, specimen A for instance was coded 99A etc.). Coded specimens were placed in appropriately labeled specimen trays which identified each specimen in batch-letter format. All specimens were notched using a notching rig and checked for notch quality consistency using an optical microscope at 75x magnification.

The following figure illustrates the treatment sequence of specimens within the experiment following a singular batch. In the experiment the three batches shared oven time as treatment to maintain treatment consistency. All three levels of thermal treatment were maintained for a constant amount of time along with constant time of “out-life” or time spent in the desiccator while not in treatment.

![Figure 10: Experimental design used to evaluate self-healing of HUB based polymers.](image)

For batches in which a larger number of specimens were available treatment levels were added to the study such as room temperature and slightly elevated temperature levels. Treatment levels and their designators are shown in table 1.
Table 1: Experimental Treatment Levels, T-Tₜ Study, XDI-0

<table>
<thead>
<tr>
<th>Treatment ID</th>
<th>Treatment:</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>Initial specimen failure, coded “0” as numerical ID required for statistical analysis using Minitab.</td>
</tr>
<tr>
<td>23</td>
<td>23°C (Room Temperature), stored in desiccator for 48 hours.</td>
</tr>
<tr>
<td>32</td>
<td>32°C oven treatment for 12 hours, stored in desiccator for 36 hours.</td>
</tr>
<tr>
<td>60</td>
<td>60°C oven treatment for 12 hours, stored in desiccator for 36 hours.</td>
</tr>
<tr>
<td>70</td>
<td>70°C oven treatment for 12 hours, stored in desiccator for 36 hours.</td>
</tr>
<tr>
<td>80</td>
<td>80°C oven treatment for 12 hours, stored in desiccator for 36 hours.</td>
</tr>
</tbody>
</table>

This experimental setup is designed to allow for ANOVA and pairwise comparisons among treatment levels to establish a relationship between temperature treatment and healing efficiency thus allowing for the testing of H₂. This experimental design also allows for testing of H₁ by comparing Level 0 to treatment levels attributed to thermal acceleration of the self-healing process. H₁ may be confirmed by the lack of a statistical difference in means between new and healed specimen strengths through overlapping pairwise groupings at the 95% confidence level.

H₁ and H₂ are quantitative experiments allowing for statistical confirmation of hypotheses. H₃ however is the consideration of a technology demonstration effort and the determination if its success relies on the examination of the laminate produced using standard composite manufacturing techniques using qualitative inspection. The requirements for H₃ confirmation as follows:

- Laminate must be producible using common commercially available fiber reinforcement (CF, Fiberglass, or Kevlar)
- Laminate must not show any evidence of major defects (Bubbles, lack of wet-out, uneven laminate thickness)
- Laminate must be producible using standard single sided vacuum bagging process using standard materials is described by the FAA Airframe Handbook, Chapter 7. (FAA,AMT CH7)
CHAPTER 3: Synthesis of Polymer

3.1: Polymer Synthesis Overview
Polymer synthesis is intended to allow for the manufacture of a neat HUB containing resin that can be used to cast tensile testing specimens to test $H_1$ and $H_2$ while also allowing for the impregnation of fiber reinforcements in order to test $H_3$. The creation of a 2-part resin system is ideal for utilization in wet-layup composites. The system produced is a 2-part system activated by a catalyst. The two primary parts of the system proposed are a Pre-Polymer which contains the HUB groups and a mixture of chain extenders in the form of diols (TEG) and crosslinking sites in the form of trifunctional groups (TEA) allowing for the formation of a 3D crosslinked network upon polymer cure.

This is a single pot synthesis in which first pre-polymer is formed giving the desired balance of aromatic to aliphatic pre-polymer constituents followed by the addition of the chain extenders and crosslinking sites. Catalyst is then added, at which point the polymer solution may be cast in the form of a neat resin as needed.

An illustrated representation of the polymer formation process is shown in the following sequence of diagrams 12-14. The first step, the formation of the pre-polymer is where TBEU is dropwise incorporated into a mixture of isocyanates. Figure 12 (A) shows the formation of a fully aliphatic prepolymer which is used to produce an XDI-0 polymer.

![Figure 11: N,N’-Bis(tert-butyl)ethylenediamine (1,2-Bis(tert-butylamino)ethane) (TBEU)](image-url)
The formation of the pre-polymer is where the HUB sites are established between the hindered diamines and the isocyanates. This establishes the “weak link” in the chain where disassociation and re-association occur allowing for the self-healing process (Ying et al, 2014). After the pre-polymer constituents are mixed a pre-polymer is allowed to form with an excess of isocyanates allowing for the theoretical limitation of MW a solution of low MW pre-polymer due to the excess of isocyanates.
Figure 13 represents the addition of the TEA and TEG forming extended polymer chains allowing for crosslinking to occur between the excess isocyanate groups and hydroxyl groups on the diols and trifunctional groups.

![Figure 13: Representation of chain extension and crosslinking of an aliphatic prepolymer](image)

Figure 13 serves as a representation of chain extension and crosslinking of an aliphatic prepolymer forming an aliphatic HUB containing network, which in this study is labeled as XDI-0. These extended chains may then form a network structure of a prescribed crosslink density, as controlled by addition of TEA is a critical consideration in the design of this polymer. Due to this a constant TEA/TEG ratio has been used in this research.

### 3.2: Pre-Polymer Solubility
The pre-polymer base of all polymers investigated in this research consists of TBEU and diisocyanates with the ideal prepolymer being three constituent units long consisting of TBEU and two diisocyanates forming two instances of a Hindered Urea Bond (HUB). The creation of this pre-polymer is the first step to each synthesis and what defines the polymer’s aromatic content.
It was previously held to be fact that in order to create a homogenous blend of diisocyanates and TBEU a solvent needed to be added in order to dilute the mixture allowing for the formation of a low MW pre-polymer. In order to dilute the solution two solvents were tried. Firstly Dimethyl formamide (DMF, anhydrous) was used as a diluent with the work of (Bruce, Lewis, 2017).

In order to reduce the chances of water contamination DMF was replaced by distilled toluene. Distilled toluene proved capable of allowing for a homogenous pre-polymer to be created without allowing for the formation of long polymer chains which became visible as they were spun into a “cotton candy” appearance entangling the stir-bar within the synthesis vial despite the excess of NCO groups in the pre-polymer solution.

This creation of “cotton candy”, or visible polymer phase separated out of solution was initially thought to only be circumvented through large amounts of solvent in order to decrease the likelihood of bond formation and to thin the viscosity of the mixture to allow for mixing into a homogenous pre-polymer. However in one XDI-75 batch attempt in which limited Toluene was used and phase separated polymer had begun to form the stir rate was set from “4” up to “10” as the batch was presumed scrapped so an impromptu experiment took place by increasing stir rate. The phase separated polymer then dissipated and appeared to go back into solution in the rapid stirring conditions present in the vial.

Before this observation stir rate had never been considered as a main factor worth considering in the polymer synthesis as focus was placed on other factors in the experiment. Given this observation for the following several syntheses toluene was used as a diluent and stir rates were held in the “7-10” (rapid-turbulent) regime in which a turbulent whirlpool was active within the synthesis vial. With toluene as acting diluent and a high stir rate successful formation of a
homogenous, clear pre-polymer was accomplished and used to produce high quality polymer specimens.

However successful synthesis of high quality specimens using large amounts of toluene lead to related issues with the later removal of toluene through drying process a subject of further discussion. It was however found that the pre-polymer could be created without phase separation through aggressive viscous shear as a replacement for toluene all together leading to successful toluene free syntheses.

3.3: Water Reactions & Atmospheric Moisture
Achieving homogeneous, bubble-free samples was a struggle, particularly in the early stages of sample preparation. Water was considered the main cause of bubble-defects as the presence of isocyanate-water reactions producing CO₂ in gaseous form was suspected (Kent, 2007, p. 608). Due to the concern of the water reaction both from a synthetic standpoint by producing ureas and using up NCOs instead of forming HUBs and the bubble production an evaluation of water content of each chemical constituent was performed using Karl Fisher Titration. Results from KF titration are as follows:

<table>
<thead>
<tr>
<th>Chemical:</th>
<th>TBEU</th>
<th>TEA</th>
<th>TEG(NEW)</th>
<th>TEG(Dried)</th>
<th>DMF</th>
<th>Toluene (New dist)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trial 1:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>% Water by weight</td>
<td>0.073</td>
<td>0.180</td>
<td>0.274</td>
<td>1.331</td>
<td>1.290</td>
<td>0.004</td>
</tr>
<tr>
<td>Volume Tested:</td>
<td>~1.5ml</td>
<td>~1.5ml</td>
<td>~1ml</td>
<td>~1.5ml</td>
<td>~5ml</td>
<td>~5ml</td>
</tr>
<tr>
<td>Mass Tested (grams):</td>
<td>1.0</td>
<td>1.8</td>
<td>0.1</td>
<td>0.9</td>
<td>4.4</td>
<td>4.0</td>
</tr>
<tr>
<td>Mass of Water In sample (Micrograms)</td>
<td>733</td>
<td>3181</td>
<td>373</td>
<td>11536</td>
<td>56586</td>
<td>168</td>
</tr>
</tbody>
</table>

From the Karl Fisher Titration it was found that our solvent of primary use, DMF was contributing a significant amount of water along with TEG. At the point of this observation the
solvent of choice shifted from DMF to that of distilled toluene in order to avoid the introduction of water through solvent addition.

Drying protocols were then established in order to reduce the water content introduced by TEG and TEA through the storage of small amounts of the chemicals in 100ml round bottom flasks containing activated 3A molecular sieves. The flasks containing the chemicals in order to maintain a minimal exposure to water were sealed with septums and purged with dry (desiccated Drierite® Drying Tube (300mL/min in line desiccator) nitrogen gas to remove any air that may contain atmospheric moisture. After the introduction of dried TEA and TEG through the use of 3A molecular sieves along with the transition to toluene as a solvent for pre-polymer dilution sample quality improvements were observed in terms of bubble content.

Whenever possible steps were taken in order to eliminate the introduction of atmospheric moisture to the synthesis vial. However moisture prevention measures occurred before synthesis by the oven-treatment of all lab ware and instruments involved in the synthesis. Before any synthesis the needles, stir bars, synthesis vials, vial caps, septums, syringes, and dogbone molds were held above 100 °C for a minimum of 20 minutes at atmospheric pressure to boil off any moisture that associated with the equipment’s ambient storage conditions.

3.4: Catalyst Selection:

Prior work (Bruce, Lewis, 2017) used DBTDA (dibutyltin diacetate) as a catalyst for all formulations. Further concern over water reactions lead towards the transition towards the usage of KKAT-6212, a zirconium chelate based urethane catalyst. Cause for this transition was due to a high selectivity of NCO and OH reactions (King Industries, 2009) as opposed to undesirable NCO and H₂O reactions thought to be occurring and leading to the formation of CO₂ gas and
subsequent bubble defect formation within the samples. The transition from DBTDA to KKAT-6212 was observed to lead towards further improvements in sample quality.

3.5 Synthesis Procedure
All glassware and associated hardware was heated above 100°C for 20-30 minutes to drive off any condensed moisture to avoid contamination of the synthesis with “wet” glassware.

The chemicals stored in the refrigerator (TBEU, HMDI, XDI) are retrieved and remained sealed until they came up to room temperature.

Setup is done in parallel with glassware treatment, once glassware had been heated to remove moisture the round bottom flask (RBF) is then sealed using a rubber septum after inserting stir-bar. Silicone molds are then placed into vacuum oven at 25 inches of mercury and held under vacuum until later vacuum oven usage is required to maintain moisture-free molds.

Pre-polymer formation consists of the addition of hexamethylene diisocyanate (HMDI) and m-xylene diisocyanate (XDI) into the RBF followed by the dropwise incorporation of TBEU while undergoing very rapid stirring using the magnetic stir bar.

Once all TBEU is added it is critical to maintain rapid mechanical stirring of pre-polymer solution, adjustment to stir speed may be needed but maintaining the turbulent vortex inside of RBF is crucial. Allow to mix for 5 minute while TEA/TEG mixture is prepared in following steps.

The TEA/TEG mixture is then made in parallel in a separate transfer vial, mixed and added to the pre-polymer solution under an inert nitrogen flow acting as shield gas. The RBF containing the pre-polymer and TEA/TEG mixture is then brought into the vacuum oven and de-gassed while undergoing stirring at 25 inHg vacuum until bubbles had dissipated and clear polymer
solution remains. After degassing, the solution can then be returned to the hood and nitrogen shield reapplied.

A charge of catalyst is then prepared for addition to the solution, before addition of catalyst the solution should be brought to a turbulent mix for a short period of time followed by the injection of catalyst into the center of the turbulent vortex induced by the stir bar. 5 seconds mixing time is then allowed prior to casting polymer into molds.

Molds filled with polymer solution are then inserted into the vacuum oven. Vacuum is then applied to the chamber until 10inHg of vacuum is attained allowing flow of dry nitrogen into vacuum chamber slowly maintaining 5-10 inHg of vacuum for 30 seconds. Vacuum is then shut off and nitrogen is allowed to fill the chamber acting as a shield gas. Once ambient pressure is reached the sealed chamber is left overnight for 24 hours. The polymer can then be removed from the molds as a bulk material sample, at which point it is left in ambient conditions in the desiccator for another 24 hours. The polymer is then post-cured for 24 hours at 60°C in sealed vacuum oven at standard pressure.

3.6: XDI-0 Synthetic Formulation
The following synthesis allows for an ideal yield of 11.3ml of XDI-0 polymer. This reaction runs in slight excess of isocyanates as despite efforts to reduce the contamination of the synthesis with moisture an excess of isocyanates has been maintained to allow for “sacrificial” NCO end groups. Another consideration of added NCO groups is to allow for the healing interface or polymer itself to not be effected by hydrolysis with atmospheric moisture.

Beyond slight excess of NCO equivalent end groups a near stoichiometric balance of 1.022:1 of NCO: NH&OH groups has been chosen. Prepolymer consists of HMDI (NCO contributor) and TBEU (NH contributor) in 3:1 ratio to allow for low molecular weight prepolymer formation as
the TBEU diamine will be overcome with such as excess of NCO groups an idealized pre-polymer should be attainable. XDI-0, a fully aliphatic polymer was produced using the following reagent amounts to produce repeatable high quality polymer synthesis using 0.9% KKAT 6212 as catalyst.

Table 3: XDI-0 Synthesis Formulation Amounts

<table>
<thead>
<tr>
<th>CHEMICAL</th>
<th>GROUP TYPE</th>
<th>GROUPS</th>
<th>Volume(ml)</th>
<th>Mass(g)</th>
<th>Density</th>
<th>MW (g/mol)</th>
<th>mols (calc)</th>
<th>mol-groups*10^3</th>
<th>TOTALS</th>
</tr>
</thead>
<tbody>
<tr>
<td>HMDI</td>
<td>NCO</td>
<td>2</td>
<td>5.256</td>
<td>5.50303</td>
<td>1.047</td>
<td>168.19</td>
<td>3.27E-02</td>
<td>65.44</td>
<td></td>
</tr>
<tr>
<td>TBEU</td>
<td>NH</td>
<td>2</td>
<td>2.356</td>
<td>1.82244</td>
<td>0.799</td>
<td>172.31</td>
<td>1.09E-02</td>
<td>21.85</td>
<td></td>
</tr>
<tr>
<td>TEA</td>
<td>OH</td>
<td>3</td>
<td>0.36</td>
<td>0.26136</td>
<td>0.726</td>
<td>149.15</td>
<td>1.73E-03</td>
<td>5.26</td>
<td></td>
</tr>
<tr>
<td>TEG</td>
<td>OH</td>
<td>2</td>
<td>3.188</td>
<td>3.5865</td>
<td>1.175</td>
<td>194.23</td>
<td>1.85E-02</td>
<td>36.93</td>
<td></td>
</tr>
</tbody>
</table>

Using this formulation the tensile specimens in the following image were produced and used for the second hypothesis (H2) testing involving the T-Tg effect of XDI-0.

![Figure 14: XDI-0 Yield](image)

Further experimentation with XDI-0 production resulted batch 101 which was used to determine the quality of the resin in producing a laminate and for producing bulk samples as shown in figure 16 as 2” diameter, 0.72” polymer disks.

![Figure 15: Target samples and PMC laminate, made using a HUB based polymer (XDI-0)](image)
3.7: XDI-25 Synthetic Formulation
The following synthesis allows for an ideal yield of 2.8ml of XDI-25 polymer, using 0.75% KKAT 6212 as catalyst. The amounts shown have been doubled to produce 11 tensile testing specimens.

<table>
<thead>
<tr>
<th>CHEMICAL</th>
<th>GROUP TYPE</th>
<th>GROUPS</th>
<th>Volume(ml)</th>
<th>Mass(g)</th>
<th>Density</th>
<th>MW(g/mol)</th>
<th>mols (calc)</th>
<th>mol<em>groups</em>1000</th>
<th>GROUP mol*10^3 TOTALS</th>
</tr>
</thead>
<tbody>
<tr>
<td>XDI</td>
<td>NCO</td>
<td>2</td>
<td>0.321</td>
<td>0.38584</td>
<td>1.202</td>
<td>188.19</td>
<td>2.05E-03</td>
<td>4.10</td>
<td></td>
</tr>
<tr>
<td>HMDI</td>
<td>NCO</td>
<td>2</td>
<td>0.985</td>
<td>1.0313</td>
<td>1.047</td>
<td>168.19</td>
<td>6.13E-03</td>
<td>12.26</td>
<td></td>
</tr>
<tr>
<td>TBEU</td>
<td>NH</td>
<td>2</td>
<td>0.589</td>
<td>0.47061</td>
<td>0.799</td>
<td>172.31</td>
<td>2.73E-03</td>
<td>5.46</td>
<td></td>
</tr>
<tr>
<td>TEA</td>
<td>OH</td>
<td>3</td>
<td>0.09</td>
<td>0.06534</td>
<td>0.726</td>
<td>149.19</td>
<td>4.38E-04</td>
<td>1.31</td>
<td></td>
</tr>
<tr>
<td>TEG</td>
<td>OH</td>
<td>2</td>
<td>0.797</td>
<td>0.89663</td>
<td>1.125</td>
<td>194.23</td>
<td>4.62E-03</td>
<td>9.23</td>
<td></td>
</tr>
</tbody>
</table>

In XDI containing polymers such as XDI-25 minor phase separation and bubble defects have prevailed using current synthesis procedures. One explanation for such issues is that of atmospheric moisture contamination resulted in minor amounts of CO₂ production.

![Figure 16: XDI-25 Yield](image)

3.8: XDI-50 Synthetic Formulation
The following synthesis allows for an ideal yield of 2.8ml of XDI-50 polymer, using 0.75% KKAT 6212 as catalyst. XDI-50 was found to also have bubble defect issues and apparent phase separation.

<table>
<thead>
<tr>
<th>CHEMICAL</th>
<th>GROUP TYPE</th>
<th>GROUPS</th>
<th>Volume(ml)</th>
<th>Mass(g)</th>
<th>Density</th>
<th>MW(g/mol)</th>
<th>mols (calc)</th>
<th>mol<em>groups</em>1000</th>
<th>GROUP mol*10^3 TOTALS</th>
</tr>
</thead>
<tbody>
<tr>
<td>XDI</td>
<td>NCO</td>
<td>2</td>
<td>0.643</td>
<td>0.772886</td>
<td>1.202</td>
<td>188.19</td>
<td>4.11E-03</td>
<td>8.21</td>
<td></td>
</tr>
<tr>
<td>HMDI</td>
<td>NCO</td>
<td>2</td>
<td>0.657</td>
<td>0.687879</td>
<td>1.047</td>
<td>168.19</td>
<td>4.09E-03</td>
<td>8.18</td>
<td></td>
</tr>
<tr>
<td>TBEU</td>
<td>NH</td>
<td>2</td>
<td>0.589</td>
<td>0.47061</td>
<td>0.799</td>
<td>172.31</td>
<td>2.73E-03</td>
<td>5.46</td>
<td></td>
</tr>
<tr>
<td>TEA</td>
<td>OH</td>
<td>3</td>
<td>0.09</td>
<td>0.06534</td>
<td>0.726</td>
<td>149.19</td>
<td>4.38E-04</td>
<td>1.31</td>
<td></td>
</tr>
<tr>
<td>TEG</td>
<td>OH</td>
<td>2</td>
<td>0.797</td>
<td>0.89663</td>
<td>1.125</td>
<td>194.23</td>
<td>4.62E-03</td>
<td>9.23</td>
<td></td>
</tr>
</tbody>
</table>

![Table 5: XDI-50 Synthesis Formulation Amounts](image)
3.9: XDI-75 Synthetic Formulation

The following synthesis allows for an ideal yield of 5.5ml of XDI-75 polymer, using 0.75% KKAT 6212 as catalyst. One item to note when planning synthesis of XDI-75 is that due to the viscous nature of a highly aromatic polymer solution one should expect a significant proportion of the polymer yield potential to remain in the pot as transfer losses when casting small amounts of the polymer. This is especially true when large reaction vessels are used for small synthesis quantities.

Table 6: XDI-75 Synthesis Formulation Amounts

<table>
<thead>
<tr>
<th>CHEMICAL</th>
<th>GROUP TYPE</th>
<th>GROUPS</th>
<th>Volume</th>
<th>Density</th>
<th>MW (g/mol)</th>
<th>mols (calc)</th>
<th>mol:groups*1000:</th>
<th>GROUP mol*10^3 TOTALS:</th>
</tr>
</thead>
<tbody>
<tr>
<td>XDI</td>
<td>NCO</td>
<td>2</td>
<td>1.928</td>
<td>1.202</td>
<td>188.19</td>
<td>1.23E-02</td>
<td>24.63</td>
<td></td>
</tr>
<tr>
<td>HMDI</td>
<td>NCO</td>
<td>2</td>
<td>6.356</td>
<td>1.047</td>
<td>168.19</td>
<td>4.08E-03</td>
<td>8.17</td>
<td></td>
</tr>
<tr>
<td>TBEU</td>
<td>NH</td>
<td>2</td>
<td>1.178</td>
<td>0.799</td>
<td>172.31</td>
<td>5.46E-03</td>
<td>10.92</td>
<td></td>
</tr>
<tr>
<td>TEA</td>
<td>OH</td>
<td>3</td>
<td>6.18</td>
<td>0.726</td>
<td>149.19</td>
<td>8.76E-04</td>
<td>2.63</td>
<td></td>
</tr>
<tr>
<td>TEG</td>
<td>OH</td>
<td>2</td>
<td>1.594</td>
<td>1.125</td>
<td>194.23</td>
<td>9.23E-03</td>
<td>18.47</td>
<td></td>
</tr>
</tbody>
</table>

The following image shows XDI-75 tensile specimens after the post-curing process (24 hours, 60°C). The specimens had some bubble defects however the majority of the white appearance is hypothesized to be from where the surface of the specimens was in contact with the glass slide during curing causing entrapped air to mar the surface of the specimen.
3.10: Thermal Limitations on Post-Treatment & Residual Toluene on Polymer T\textsubscript{g}:

Polymers synthesized utilizing toluene have led to great experimental difficulty as these polymers exhibit T\textsubscript{g}’s well below that expected. Closer to expected T\textsubscript{g}’s were achieved through thoroughly baking out samples, however in order to do so the samples became discolored and bubbles had been enlarged. The problem here is that the actual T\textsubscript{g} of specimens characterized via mechanical testing is much lower than the T\textsubscript{g} of baked samples due to the presence of toluene in the former. Previous work (Bruce, Lewis, 2017) involved elevated temperature post-curing the samples but this post-curing process was found to be insufficient in removing all residual solvent. The efficiency of toluene removal via vacuum drying was evaluated on specimens containing 34 and 39 mol\% XDI

XDI-50 was found to exhibit a T\textsubscript{g} of 20°C in prior work (Bruce, Lewis, 2017). An evaluation of the process capability of the current drying process (60°C, 24hours, -25inhg) resulted in a T\textsubscript{g} of 7.06°C. Due to this lower than expected Tg the sample was then placed back into the same treatment for another 48 hours, resulting in a total treatment time of 72 hours at the prescribed 60°C, 24hours, -25inhg treatment resulting in a T\textsubscript{g} of 7.53°C.
As the drying process of 60°C for 24 hours in the vacuum oven at -25 inhg did not remove all toluene an experiment of increasing the temperature while holding the time constant was done to determine if the drying process could be done without added time or degrading sample quality.

XDI-75 expected to have a $T_g$ of 30°C (Bruce, Lewis, 2017). FTIR results of the polymer found a local minimum value of 98.79% transmission (between 2500 cm$^{-1}$ and 2200 cm$^{-1}$) at a wavelength of 2335 cm$^{-1}$ where NCO groups would be expected to be found at 2270 cm$^{-1}$ (S. Kinugasa, K. Tanabe and T. Tamura). This result allowed the confirmation that there was a negligible amount of residual isocyanate remaining.

Three samples containing 75 mol% XDI were subjected to various treatment conditions to assess their influence on toluene removal. Presence of toluene considered cause of reduced $T_g$ of polymers. Extraction of toluene through oven drying and corresponding $T_g$ are shown in table 7.

*Table 7: XDI-75, Study of Drying & $T_g$ by Treatment*

<table>
<thead>
<tr>
<th>Sample:</th>
<th>Temperature ($^\circ$C):</th>
<th>Time (Hrs.):</th>
<th>$T_g$ ($^\circ$C):</th>
<th>Post-Treatment Sample Condition:</th>
</tr>
</thead>
<tbody>
<tr>
<td>76T*</td>
<td>Control (23)</td>
<td>N/A</td>
<td>-2.81</td>
<td>Control, No effects noted from room temp storage.</td>
</tr>
<tr>
<td>76W</td>
<td>70</td>
<td>24</td>
<td>7.24</td>
<td>Clear, Minor bubble addition or growth observed.</td>
</tr>
<tr>
<td>76W*</td>
<td>70</td>
<td>48</td>
<td>10.04</td>
<td>Clear, Minor bubble addition or growth observed.</td>
</tr>
<tr>
<td>76U</td>
<td>80</td>
<td>24</td>
<td>11.97</td>
<td>Slightly yellowed, small bubble additions noted</td>
</tr>
<tr>
<td>76V</td>
<td>90</td>
<td>24</td>
<td>21.98</td>
<td>Yellowed, Bubble growth observed.</td>
</tr>
</tbody>
</table>

*Indicates part of follow-up study*
Treatment at 70°C was found to be the least damaging to the specimen, however 24 hours at 70°C was only found to increase the polymers T_g by 10.05°C to 7.24°C, still far below the theoretical maximum T_g of 30°C. Treatment at 90°C resulted in damage to the specimen resulting in a T_g of 21.98°C, still below of the theoretical 30°C (Bruce, Lewis, 2017).

Table 8: Specimen Degradation & Thermal Treatment

<table>
<thead>
<tr>
<th>Specimen Degradation &amp; Treatment</th>
<th>Pre-Treatment: 70°C, 24hours, Standard Pressure</th>
<th>Post Treatment:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specimen Degradation</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Treatment:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>80°C, 24hours, Standard Pressure</td>
<td></td>
<td></td>
</tr>
<tr>
<td>90°C, 24hours, Standard Pressure</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Due to the results of this study it was found that the synthetic technique using toluene and the subsequent drying process was incapable of producing toluene free samples. Since it was our goal to prepare networks with the highest possible T_g's we elected to pursue a solvent free synthetic procedure.

3.11: Effect of Post Curing on Polymer T_g:
Polymer T_g after synthesis was found to be lower than the expected results. Previous experimentation (Bruce, Lewis, 2017) had found the averaged T_g of the polymers when fully baked out to remove toluene, however in order to attain these T_g's the polymer had been destroyed in the process by thermal degradation, thus resulting in the lack of test-quality samples at the expected T_g.
A Post-curing process was considered necessary to attain greater $T_g$ in specimens closer to the expected $T_g$. The following table outlines DSC data from this study:

Table 9: Effect of Post Curing on Polymer $T_g$.

<table>
<thead>
<tr>
<th>Polymer Type (Aromatic Content)</th>
<th>$T_g$ Expected (°C)</th>
<th>$T_g$ Post Synthesis, prior to post-cure (°C)</th>
<th>$T_g$ Post Cured, [24 hours 60° C] (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>XDI-0 No Toluene</td>
<td>-5</td>
<td>-1.75</td>
<td>5.70</td>
</tr>
<tr>
<td>XDI-25 No Toluene</td>
<td>10</td>
<td>-0.64</td>
<td>6.32</td>
</tr>
<tr>
<td>XDI-50 No Toluene</td>
<td>20</td>
<td>13.39</td>
<td>20.73</td>
</tr>
<tr>
<td>XDI-75 No Toluene</td>
<td>Not in Study (Bruce, Lewis, 2017)</td>
<td>22.30</td>
<td>29.70</td>
</tr>
</tbody>
</table>

One item noticed in the evaluation of toluene free specimens used for tensile testing was that the XDI-0 and XDI-25 showed similar $T_g$’s which does not agree findings of prior work (Bruce, Lewis, 2017). However this disagreement is to be expected as major changes in synthetic technique including the lack of using solvents for synthesis is thought to contribute to varied mechanical properties inclusive of $T_g$. The residual solvent in samples using toluene is a plausible explanation for lower $T_g$’s experience in prior work however this explanation is only logically applicable to XDI-0. The action of post-curing effecting the $T_g$ of the polymers can be attributed to chain mobility as elevated temperatures during post cure allowing for unreacted groups to become mobile and react forming a network with a higher crosslink density than previously established before post-curing.
3.12 Manufacture of PMC Laminate Using HUB based Matrix Material
In order to demonstrate the feasibility of the manufacture of a fiber reinforced PMC laminate (H3) using the vacuum bagging process a 5-ply 0/90 degree laminate \([0/90]_5\) using 4 Harness-Satin woven Kevlar from Soller Composites (Soller Composites, 2018) was produced using a common composites hand layup technique followed by vacuum bagging consolidation.

Kevlar plies were prepared along with a peel ply, perforated ply, and a breather ply. An aluminum tool treated with Rain-X ® Original Glass Water Repellant (manufactured by ITW Global) as a release agent was prepared with bag sealant tape. Polymer synthesis of XDI-0 was performed per the procedure outlined in chapter 3. Following addition of catalyst to the polymer the near resin was deposited onto the surface of the dry fiber reinforcements on the tool and wet-out using a squeegee. After fiber wet out the vacuum bag was sealed promptly and the laminate was consolidated through application of 25inhg vacuum and left under vacuum overnight to at room temperature to cure.

*Figure 19: Vacuum Bagging Materials, Kevlar \([0/90]_5\), Peel Ply, Perf Ply, Breather Ply, Bag*
The bagging materials were removed from the tool leaving the cured laminate on the tool as shown in the following images both prior and post trimming of the laminate. Given the Kevlar/XDI-0 laminate it was found difficult to trim using conventional methods and the use of carbide nibblers were employed to trim the laminate to final form. Please note that black on laminate edges is residual from use of marker usage in fabric layout.
Figure 22: Trimmed Kevlar \([0/90]_5\) Laminate, Toolside

Figure 23: Trimmed Kevlar \([0/90]_5\) Laminate, Bagside
CHAPTER 4: Mechanical Characterization & Self-Healing

4.1: Initial Mechanical Properties
Mechanical properties of the new, notched specimens are represented in the following table with all values attributed to failure of the specimen.

Table 10: Polymer Initial Material Properties Averages

<table>
<thead>
<tr>
<th>XDI CONTENT</th>
<th>Strain at Break (%)</th>
<th>Stress at Break (psi)</th>
<th>Modulus (psi)</th>
<th>Energy (ft-lbf)</th>
<th>Tg (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>606%</td>
<td>476.0</td>
<td>168.0</td>
<td>0.533</td>
<td>5.70</td>
</tr>
<tr>
<td>25</td>
<td>477%</td>
<td>856.0</td>
<td>311.0</td>
<td>0.799</td>
<td>6.32</td>
</tr>
<tr>
<td>50</td>
<td>20.0%</td>
<td>2844</td>
<td>38800</td>
<td>N/A</td>
<td>20.73</td>
</tr>
<tr>
<td>75</td>
<td>14.0%</td>
<td>6467</td>
<td>120500</td>
<td>0.186</td>
<td>29.70</td>
</tr>
</tbody>
</table>

One noteworthy item in table 10 is the distinct difference between XDI-0, XDI-25 and XDI-50, XDI-75 specimens in regard to mechanical properties. The large differences in material properties is thought to be attributed to the $T_g$’s of the polymers with respect to their testing at 23°C as room temperature. During tensile testing it was observed that samples with low XDI content exhibited a high elongation at break and plastic deformation followed by a high degree of necking followed by failure whereas XDI-50 and XDI-75 exhibited low elongation at failure followed by a failure mechanism resembling crack propagation in a brittle medium with very little necking before failure.

Figures 24-27 display the observed trends in relation to XDI content of the polymers and their initial mechanical properties.
Figure 24: Failure Stress (Untested Specimens) as a function of XDI concentration

Figure 25: Failure Strain (Untested Specimens) as a function of XDI concentration
Figure 26: Glass transition temperature (Tg) as a function of XDI concentration

Figure 27: Young’s Modulus (Untested Specimens) as a function of XDI concentration
4.2: Comparison of Initial Mechanical Properties by Research

Development of HUB based polymers and the overlapping research among recent work is presented in the following table as an examination of differences among researchers.

Table 11: Comparison of Material Properties (by researcher, standard cross section)

<table>
<thead>
<tr>
<th>XDI-Content</th>
<th>Researcher</th>
<th>Strain (%)</th>
<th>Stress(MPa)</th>
<th>E-MOD(MPa)</th>
<th>Tg</th>
</tr>
</thead>
<tbody>
<tr>
<td>XDI-0</td>
<td>Ying et al.</td>
<td>426%</td>
<td>0.93</td>
<td>1.22</td>
<td>-52</td>
</tr>
<tr>
<td></td>
<td>Bruce, Lewis</td>
<td>385%</td>
<td>3.07</td>
<td>1.30</td>
<td>-5</td>
</tr>
<tr>
<td></td>
<td>Schevtchuk</td>
<td>606%</td>
<td>3.28</td>
<td>1.16</td>
<td>6</td>
</tr>
<tr>
<td>Difference</td>
<td>(Bruce-Schevtchuk)</td>
<td>36%</td>
<td>6%</td>
<td>-12%</td>
<td></td>
</tr>
<tr>
<td>XDI-25</td>
<td>Bruce, Lewis</td>
<td>345%</td>
<td>4.91</td>
<td>3.89</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>Schevtchuk</td>
<td>477%</td>
<td>5.90</td>
<td>2.15</td>
<td>6</td>
</tr>
<tr>
<td>Difference</td>
<td>(Bruce-Schevtchuk)</td>
<td>28%</td>
<td>17%</td>
<td>-81%</td>
<td></td>
</tr>
</tbody>
</table>

Prior work (Ying et al., 2014) provided the basis for the understanding of HUBs and proved the capability to prepare low T_g self-healing polymers using HUBs with desirable healing efficiencies. This work however produced polymeric gels with limited application.

Work done by (Bruce, Lewis 2017) expanded the capability of the preparation of HUB based polymers to include polymers with T_g’s above 0°C and provided evidence towards the relationship between aromatic content and healing efficiency at constant healing conditions (60°C/12h).

Continued research presented in this study goes on to study the healing efficiencies of these polymers with healing temperature as a major consideration.

Improvements in polymer synthesis technique allowed for the preparation of higher quality specimens. This resulted in tensile testing difficulties never experienced in prior work such as jaw slippage as the new polymers are tougher showing 36% increase in strain at failure for XDI-0 and 6% increase in strength when comparing notched specimens to non-notched specimens.
Major improvements in polymer toughness is attributed to decrease in random stress concentrations due to bubbles, the removal of residual solvent and a more complete crosslinking.

Our improved sample preparation technique had an unintended consequence: New, untested specimens were not able to be taken to failure as a result of slippage in the jaws. Thus it was necessary to notch our specimens prior to tensile testing. The notching of the specimens can best be approximated as a crack in a finite plate in uniaxial loading resulting in a normal opening or Mode 1 failure (Roylance, D., 2001). A recommended specimen geometry for future tests may be the ASTM D638 Type IV tensile testing dogbone (ASTM D638-02A) as it contains a much narrower gauge section relative to the grip surface area.

Several assumptions may however be made to allow for an approximation to allow for a generalized stress concentration formula to be used to determine stress at the notch tip. One must assume that the material does not allow for plastic work to allow for a redistribution of stresses in which a more uniform stress distribution may occur. One must also assume that the notch may be considered a crack in which the \( \rho_t \), the radius of curvature of the crack tip may be approximated as half the width of the notch with notch depth analog to crack depth. It must also be assumed that the material yields leading to failure at the localized stress corresponding to the notch or crack tip. Using dimensions from the notched specimens we find the crack trip diameter (\( \rho_t \)) to be approximated as \( \rho_t = 0.01" \), the notch depth (a) to be approximated as \( a = 0.02" \). The using the following formula we may determine the stress concentration, \( K_t \) as follows:

\[
K_t = 2 \sqrt{\frac{a}{\rho t}} = 2 \sqrt{\frac{0.02"}{0.01"}} = 2.82
\]

(Callister, W.D., 2000)
The stress concentration factor can be taken as a measure of the amplification of a stress at the notch tip. Therefore the interpretation is that the stress at the tip of the notched specimen is about 3X that of a bulk specimen. This equation is applicable to brittle materials where stresses are concentrated at the crack tip. The fact that polymers are viscoelastic in nature implies that stresses will not be concentrated at the crack tip and therefore this approximation is an exageration. Nevertheless, this simple analysis does reveal that our results should not be directly compared to previous investigators and for this reason we suggest a new tensile bar geometry be used to remove the necessity for notching in future studies.

**4.3: Self-Healing Process**

In order for self-healing to occur the specimens must be in intimate contact allowing for the disassociated HUBS to re-associate. Due to this the self-healing process used on the tensile testing specimens relied on manual re-alignment of the specimens allowing for the failure surface to be put into intimate contact. This process of manual re-alignment acts as a source of variability in the experiment as ability of a human operator to align specimens may vary resulting in improper specimen fracture alignment and a reduced healing surface area in intimate contact.

Self-Healing was performed by placing fractured half samples into intimate contact before being subject to heat treatment. The two halves were then placed on glass slides and allowed to return to their initial shape which was recovered with 2-5 minutes after testing. At which point the two halves were picked up with gloved hands to reduce the potential of oils and moisture contaminating the healing interface. The specimen halves were placed into intimate contact allowing the specimens to come to a “tack”. The “tack” was when the specimens would be healed enough to allow for handling without the specimens falling back apart. Specimens
showed signs of instantly coming to a tack when placed into contact with each other however in order to reduce the likelihood of specimens being damaged in transport and further handling this process was done for 1 minute.

Once the batch had been initially tensile tested the samples were segregated into groups by treatment as discussed in 2.4. At which point the oven, a Binder FP 53-UL Mechanical Convection Oven, was allowed to come up to the desired heat treatment temperature. Once the oven had reached the programmed set point the specimens in intimate contact were placed on glass slide and left for 12 hours. Samples were retrieved from oven and allowed to return to room temperature before handling. Specimens were then placed back into storage in the desiccator for storage until testing.

Healed specimens were found to retain a scar from where the fracture had occurred from initial tensile testing as shown in figure 29 which also shows causes of variance due to manual re-alignment of failed specimens.

*Figure 28: XDI-0 75x Magnification of Initial Interface(Left), Healed Interface Scar(Right)*
Healing of polymers with $T_g$’s above room temperature, such as XDI-75 are incapable of coming to a room temperature tack and therefore must be placed into intimate contact after exposure to elevated temperatures. This is done by placing specimen halves into the treatment oven at their treatment temperature for 10 minutes and manually tacking the specimens and then returning them to the oven for the rest of their treatment period.

The manual placing of specimens into intimate contact through the formation processes is intended to simulate the intimate contact encountered in sub-critical cracks such as those experienced in interlaminar and intralaminar matrix cracks in fiber reinforced PMC matrix materials.

4.4: Restoration of Mechanical Properties

The testing of the restoration of mechanical properties following self-healing showed their shared treatments at differing experimental levels of temperature resulted in varying efficiencies. The primary temperature levels were healing cycles at 60°C, 70°C, and 80°C for 12 hours. When specimens were available for additional levels the levels 23°C, 32°C, and 45°C were added such as in XDI-0 testing as two batches were available for greater testing breadth. For statistical
analysis the new specimens (unbroken however notched) were coded as “Treatment 0” as numerical coding variables were required. 0 refers to no healing treatment and virgin material. The metric in which healing efficiency is being measured from is that of stress at failure in psi. In order to allow for comparison among treatment groups with a small sample population of 21 specimens with only 2-6 samples per treatment without constant variances typical statistical checks for differences among groups of means such as Tukey’s test were unavailable as the assumptions of constant variance and normality were not met. Due to this the Games-Howell Simultaneous Tests for Differences of Means were performed to confirm the significance of temperature treatment on recovered stress at the 95% level of confidence.

For XDI-0 treatment groups The Games-Howell tests then provided evidence at the 95% confidence level that there are no statistically significant differences among stress at failure between new specimens and those treated at or above 60°C.
### Games-Howell Simultaneous Tests for Differences of Means

<table>
<thead>
<tr>
<th>Difference of Levels</th>
<th>Difference of Means</th>
<th>SE of Difference</th>
<th>95% CI</th>
<th>T-Value</th>
<th>Adjusted P-Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>23 - 0</td>
<td>-233.6</td>
<td>31.2</td>
<td>(-344.6, -122.6)</td>
<td>-7.50</td>
<td>0.000</td>
</tr>
<tr>
<td>32 - 0</td>
<td>-259.3</td>
<td>39.2</td>
<td>(-432.3, -86.2)</td>
<td>-6.61</td>
<td>0.009</td>
</tr>
<tr>
<td>45 - 0</td>
<td>-182.4</td>
<td>55.5</td>
<td>(-309.5, 144.6)</td>
<td>-3.29</td>
<td>0.218</td>
</tr>
<tr>
<td>60 - 0</td>
<td>-41.5</td>
<td>68.3</td>
<td>(-317.9, 234.8)</td>
<td>-0.61</td>
<td>0.994</td>
</tr>
<tr>
<td>70 - 0</td>
<td>-8.4</td>
<td>80.8</td>
<td>(-588.4, 571.5)</td>
<td>-0.10</td>
<td>1.000</td>
</tr>
<tr>
<td>80 - 0</td>
<td>-40.3</td>
<td>46.1</td>
<td>(-275.9, 195.3)</td>
<td>-0.87</td>
<td>0.959</td>
</tr>
<tr>
<td>32 - 23</td>
<td>-25.7</td>
<td>36.2</td>
<td>(-225.7, 174.3)</td>
<td>-0.71</td>
<td>0.983</td>
</tr>
<tr>
<td>45 - 23</td>
<td>51.1</td>
<td>53.3</td>
<td>(-309.8, 412.1)</td>
<td>0.96</td>
<td>0.933</td>
</tr>
<tr>
<td>60 - 23</td>
<td>192.0</td>
<td>66.6</td>
<td>(-88.7, 472.8)</td>
<td>2.88</td>
<td>0.202</td>
</tr>
<tr>
<td>70 - 23</td>
<td>225.2</td>
<td>79.4</td>
<td>(-388.3, 838.6)</td>
<td>2.84</td>
<td>0.347</td>
</tr>
<tr>
<td>80 - 23</td>
<td>193.3</td>
<td>43.5</td>
<td>(-73.2, 459.8)</td>
<td>4.44</td>
<td>0.114</td>
</tr>
<tr>
<td>45 - 32</td>
<td>76.8</td>
<td>58.4</td>
<td>(-248.7, 402.3)</td>
<td>1.31</td>
<td>0.818</td>
</tr>
<tr>
<td>60 - 32</td>
<td>217.7</td>
<td>70.8</td>
<td>(-67.0, 502.4)</td>
<td>3.08</td>
<td>0.149</td>
</tr>
<tr>
<td>70 - 32</td>
<td>250.8</td>
<td>82.9</td>
<td>(-304.1, 805.7)</td>
<td>3.03</td>
<td>0.286</td>
</tr>
<tr>
<td>80 - 32</td>
<td>219.0</td>
<td>49.6</td>
<td>(-36.1, 474.0)</td>
<td>4.41</td>
<td>0.081</td>
</tr>
<tr>
<td>60 - 45</td>
<td>140.0</td>
<td>80.9</td>
<td>(-184.0, 465.8)</td>
<td>1.74</td>
<td>0.615</td>
</tr>
<tr>
<td>70 - 45</td>
<td>174.0</td>
<td>91.7</td>
<td>(-327.7, 675.8)</td>
<td>1.90</td>
<td>0.570</td>
</tr>
<tr>
<td>80 - 45</td>
<td>142.2</td>
<td>63.2</td>
<td>(-182.9, 467.2)</td>
<td>2.25</td>
<td>0.430</td>
</tr>
<tr>
<td>70 - 60</td>
<td>33</td>
<td>100</td>
<td>(-423, 489)</td>
<td>0.33</td>
<td>1.000</td>
</tr>
<tr>
<td>80 - 60</td>
<td>1.3</td>
<td>74.8</td>
<td>(-295.4, 297.9)</td>
<td>0.02</td>
<td>1.000</td>
</tr>
<tr>
<td>80 - 70</td>
<td>-31.9</td>
<td>86.3</td>
<td>(-553.8, 490.1)</td>
<td>-0.37</td>
<td>0.999</td>
</tr>
</tbody>
</table>

*Figure 30: Games-Howell Test for Difference in Means, XDI-0*

Although sample size is limited it may be observed that a trend is evident between the restorations of mechanical properties of XDI-0 when exposed to elevated treatment temperatures as illustrated in the following main effects plots comparing material property means among various treatment levels:
Figure 31: Failure stress as a function of self-healing temperature for XDI-0 samples.

Figure 32: Failure strain as a function of self-healing temperature for XDI-0 samples.
Figure 33: Energy at failure as a function of self-healing temperature for XDI-0 samples.

For reference purposes examples of comparisons of XDI-0 tensile testing results between new and healed specimens are shown as follows for several treatment levels:

Figure 34: XDI-0 Healed Comparison Tensile Tests, 23°C (representative samples shown)
Figure 35: XDI-0 Healed Comparison Tensile Tests, 60°C (representative samples shown)

Figure 36: XDI-0 Healed Comparison Tensile Tests, 70°C (representative samples shown)
XDI-25 evaluation for failure strength recovery is the most problematic experimentally as it is believed that overcutting in notching of these specimens allowed for an artificial decrease in initial strength allowing for healed strengths to far exceed initial strength in several circumstances. Large variances in XDI-25 tensile testing are also thought to contribute towards a lack of difference in means among all treatment groups at the 95% confidence level with room temperature (23°C) excluded as it represents a singular data point. Another interesting observation with XDI-25 is the 60°C treatment which exhibits is marginal recovery.
Figure 38: Failure stress as a function of self-healing temperature for XDI-25 samples.

Figure 39: Failure strain as a function of self-healing temperature for XDI-25 samples.
Figure 40: Energy at failure as a function of self-healing temperature for XDI-25 samples.

For reference the following figures offer side-by-side comparison from tensile testing of XDI-25 specimens before and after healing.
Figure 41: XDI-25 Healed Comparison Tensile Tests, 23°C (representative samples shown)

Figure 42: XDI-25 Healed Comparison Tensile Tests, 60°C (representative samples shown)
Figure 43: XDI-25 Healed Comparison Tensile Tests, 70 °C (representative samples shown)

Figure 44: XDI-25 Healed Comparison Tensile Tests, 80 °C (representative samples shown)
XDI-75 testing provided evidence towards reduced stress recovery ratios of highly aromatic HUB based polymers when allowed to self-heal even at elevated temperatures. It is thought that the highly aromatic polymers such as XDI-75 are inefficient at self-healing as healing efficiencies in the order of 29% of recovery of stress at failure for 70°C leave little practical applications for such polymers. The following Games-Howell test confirms the clear distinct groups formed by new as opposed to healed specimens when comparing stress at failure.

<table>
<thead>
<tr>
<th>TREATMENT</th>
<th>N</th>
<th>Mean</th>
<th>Grouping</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>8</td>
<td>6467</td>
<td>A</td>
</tr>
<tr>
<td>70</td>
<td>3</td>
<td>1925</td>
<td>B</td>
</tr>
<tr>
<td>60</td>
<td>3</td>
<td>1108</td>
<td>B</td>
</tr>
</tbody>
</table>

Means that do not share a letter are significantly different.

*Figure 45: Games-Howell test, XDI-75*

Further illustration of the low healing efficiencies can be observed in the following main effects plots showing Stress, Strain, and energy at failure. Despite the lack of notable efficiencies there is still an observable trend in increasing healing efficiency with increasing treatment temperature.
Figure 46: Failure stress as a function of self-healing temperature for XDI-75 samples.

Figure 47: Failure strain as a function of self-healing temperature for XDI-75 samples.
Figure 48: Energy at failure as a function of self-healing temperature for XDI-75 samples. For reference several side-by-side comparison plots from tensile testing of XDI-75 specimens are shown below showing performance at varied treatment levels. Note data gaps are due to low sample rate with a brittle fracture occurring at high speed lower than data acquisition rate.

Figure 49: XDI-75 Healed Comparison Tensile Tests, 60°C
Figure 50: XDI-75 Healed Comparison Tensile Tests, 70°C

Figure 51: XDI-75 Healed Comparison Tensile Tests, 80°C
4.5: T-Tg Study

In the prior section it was demonstrated that there may be an observable relationship between healing temperature of a specimen and the healing efficiency in terms of stress at failure. Variability in the study combined with limited sample sizes do not allow for the establishment of a useful general linear model. However one may establish an observable trend. This may allow one to note an observation pointing towards a relationship between that departure from the Tg and the healing efficiency of HUB based polymers but additional work is required.

![T-Tg & Failure Strength Recovery](image)

*Figure 52: T-Tg Failure Strength Recovery Plot for XDI-0, XDI-25 and XDI-50 specimens*

When considering trends developed between the T-Tg and UTS recovery it becomes evident that XDI-0 and XDI-25 share similar relationships. It also becomes evident that XDI-75 exhibits a similar trend, however with greatly reduced healing efficiencies. If molecular mobility were the only factor dictating self-healing behavior then we hypothesize a strong correlation between the mean stress recovery and the departure from Tg. The Vogel-Fulchner-Tammann (VFT) equation provides a theoretical framework for the temperature viscosity relationship. Lewis, Stewart and
Anthamatten (2014) demonstrated that this relationship was responsible for shape memory behavior of poly(butyl acrylates) bearing weak hydrogen bonding pendant groups.

The VFT relationship modeling viscosity in polymers above their $T_g$'s is expected to be applicable to all polymers treated in this study. The thermal acceleration of self-healing would be expected as a function of $T-T_g$ to result in the same viscosity of each polymer resulting in the same level of chain mobility at the same $T-T_g$. For example an XDI-0 polymer with a $T_g$ of $\sim 5^\circ C$ and an XDI-75 polymer with a $T_g$ of $\sim 30^\circ C$ should have a similar viscosity at the same $T-T_g$ according to the VFT equation. This follows then that if the XDI-0 is treated at $45^\circ C$ and the XDI-75 were to be treated at $70^\circ C$ as the $T-T_g$ of $40^\circ C$ is the same in each case this viscosity effect should allow for the same chain mobility and therefore presumably similar healing efficiencies provided that the kinetics of dissociation/association are similar at the different temperatures. This however has not been observed as even at similar $T-T_g$ values we see large differences in healing efficiencies when comparing XDI-0 & XDI-25 to XDI-75.

One item of note is that the disassociation constants of HUBs containing XDI and HMDI were determined from NMR studies (Ying, Cheng, 2014) using a dilute solution as opposed to in a polymer network which severely restricts chain mobility. This leads to the consideration that other factors at play may be implied requiring future work to classify how HUBs act when constrained within a polymer network and chain mobility is reduced.
CHAPTER 5: Conclusions & Future Work

5.1: Conclusions
This work has demonstrated the feasibility of production of high quality, low $T_g$ HUB based polymers with stable mechanical properties without the use of solvent. Prior production methods of HUB based polymers required the use of solvent which lead to unstable material properties and greatly reduced elongation at break and ultimate tensile strength. Polymer development has made it clear that the HUB based polymer is extremely moisture sensitive. This led to over the course of over a year a process overhaul in which changes in chemical formulation, glassware, catalyst concentrations, and associated hardware and processing techniques were implemented. Vacuum degassing has proven vital to the production of high quality specimens which was not possible before with the use of solvents as solvents with low vapor pressures were found to boil producing more material defects than the bubbles that were being removed had caused.

Using the processes developed in this research test quality tensile testing specimens were able to be manufactured to allow for validation of three primary hypothesis.

$H_1$: The thermoset HUB based polymer will demonstrate the capability to self-heal when placed into intimate contact with itself, thus simulating the healing of intralaminar and interlaminar matrix cracking at a macro scale allowing for the evaluation of healing efficiencies of the neat resin.

Through the application of thermal stimulus to accelerate self-healing it has been shown that HUB based polymers synthesized without solvents may demonstrate the ability to self-heal while maintaining stable $T_g$s and material properties. Through pairwise comparisons using the Games-Howell test for differences in means with a 95% confidence it has been shown that healed XDI-0 and XDI-25 polymers at several treatment levels demonstrate no statistical difference in means from new specimens with healing efficiencies for failure strength shown to exceed 90% restoration. XDI-75
however has shown failure strength recoveries below 30% failure strength recovery demonstrating significant differences between new and healed specimen failure strength means at all treatment levels.

Due to this it is thought that the development of highly aromatic PMC matrix materials for structural application with desirable self-healing properties may not be feasible using this approach. Despite the lack of desirable self-healing characteristics in high aromatic polymers (XDI-75) with above ambient \( T_g \)s as required for structural applications there may be applications for low \( T_g \) PMC matrix materials with the ability to self-heal efficiently.

\[ H_2: \text{Temperature has a significant effect on healing efficiency of the HUB based polymer as a function of healing efficiency and the departure of ambient conditions from the } T_g \text{ of the polymer as } (T-T_g). \]

Through the treatment of tensile specimens as various treatment levels corresponding to the temperature in which each specimen was healed for a fixed amount of time an observable trend has been noticed between healing efficiency and the treatment temperature as one departs from the \( T_g \) of the polymer. Treatment temperature was found to be a significant factor in the recovery of failure strength at the 95% confidence level for XDI-0 where sample numbers allowed for statistical confirmation. On XDI-25 and XDI-75 due to large variances and small sample sizes statistical confirmation is unavailable however an observable trend is evident. The outcome of testing this hypothesis is the observable relationship between temperature and healing efficiency which is attributed to chain mobility as viscosity of the polymer is lowered with increased temperature exposures leading to greater healing efficiencies.
H3: The thermoset polymer containing HUBs can be manufactured using available synthetic technologies to produce a neat resin that can be used with common composite manufacturing techniques allowing for the successful production of a fiber reinforced PMC laminate. Through the development of polymers which contain no solvent and can be producible as a two-part system of a pre-polymer and diol/trifunctional mixture set off with a catalyst one may consider the feasibility of the polymer system as a low $T_g$ resin system. A major focus of this development effort was allowing for the manufacture of a self-healing neat resin. This has been demonstrated by manufacture of neat-resin disks of XDI-0, defect free dogbones, and the manufacture of a Kevlar reinforced PMC laminate with no major defects. The successful batch scaling of XDI-0 polymer resin is intended to allow for future efforts in self-healing PMC laminate studies involving test after impact studies for healed impacted laminates.

5.2: Future Work
The ability to synthesis on a repeatable basis high quality self-healing polymers is intended to provide a pathway towards greater utilization of advanced self-healing polymeric materials in a wide array of applications. Interest in several particular applications of this polymer has led to several experiments meant to lead toward future developments.
5.2.1 Shape Memory & Shape-Memory Assisted Self-Healing

One notable attribute found in highly aromatic HUB based polymers as observed in XDI-75 of several formulations on several occasions is a shape memory effect. As this polymer has an above ambient $T_g$ when it is damaged and strained it holds its deformed shape. For example a partial tensile testing specimen has been cut twice and strained and held its deformed shape. When exposed to heat using a heat gun this specimen then proceeded to return to its initial form as shown in the following sequence in which from left to right the application of heat is occurring.

![Figure 53: XDI-75 Shape Memory Effect Demonstration](image)

The experimentation leading to the discovery of this shape memory effect was when initial exploration of temperature effects of self-healing was explored. As has been shown in this research when the HUB based polymers are allowed to come into intimate contact after failure the self-healing process may begin. By a polymer being able to return to its initial form after failure it may then become able to self-heal the interfaces which had been disassociated through mechanical failure. There may lie future applications for a shape memory assisted self-healing (“SMASH”) polymer that would take advantage of the shape memory effect to allow for healing of end use polymer goods or as advanced PMC matrix materials. However more research is required as it has been shown that self-healing of the XDI-75 is less effective than its less aromatic counterparts.
5.2.2 Ballistics XDI-0

It is hypothesized that if chain length is properly controlled a polymer which exhibits a two stage failure mechanism is possible that could allow for large amounts of energy absorption. In HUB based thermoset networks failure is hypothesized to consist of a two stage process in which the network as a whole is elongated followed by the failure of HUBs. It is proposed that a sufficiently low crosslink density polymer with aliphatic isocyanates could allow for high energy absorption through long elongation at break or long elongation though the disassociation of HUB while maintaining permanent crosslinks holding the network in bulk form.

In order test the matrix in bulk form 2” discs with a 0.072” thickness were cast of XDI-0. These cast bulk samples were created as ballistics targets and were clamped using an aluminum plate bolted through to constrain the targets within a 1.5” target area with .25” surrounding clamping area along the perimeter. The specimen clamping rig is shown in figure 54 as follows:

![Figure 54: Ballistics Specimen Clamping Rig, Specimen Constrained in Rig](image)

Using a Hy-Score Model 800 spring pistol with lead Crossman .177 cal. 7.4 grain hunting pellet. The XDI-0 ballistics targets were fired upon from with 5 feet. Four shots were fired and the results as images of the targets after ballistic impacts are shown in the following composite images (figures 55-58) at 75x magnification.
Figure 55: XDI-0 Ballistics Target Composite Image, Flap Type Penetration

Figure 56: XDI-0 Ballistics Target Composite Image, Flap & Through-Hole Penetration
Figure 57: XDI-0 Ballistics Target Composite Image, No penetration 1 of 2.

Figure 58: XDI-0 Ballistics Target Composite Image, No penetration 2 of 2.
Of the four trials two had penetration, in one instance the material failed where a “flap” failure is noted. This type of failure allows for the failed surfaces to return to intimate contact allowing for self-healing. The second trial showing penetration was a through hole puncture in which material was removed thus removing the potential of healing back to a continuous film. One item however of note is the 1mm scale bar as the round that passed through the film was a .177 cal. Pettlet which is a 4.5mm diameter. In this example we see a partial flap type failure with some material removal and cracks initiating from the flap failure having returned to intimate contact.

The two instances where penetration did not occur the pellets were rejected as ricochets. From observation of slow-motion video taken during ballistics tests the polymer appears to have elongated and rebounded thus apparently absorbing a portion of the projectiles impact energy. Abrasions are present on the films which is thought to be from the rounds edge at the end of the nose tragging through the polymer as it elongated before rejection as a ricochet.

One must note that these results experienced reflect the deformation and subsequent energy absorption of a flexible elastomer. The polymer used for these ballistics tests was the XDI-0 polymer, the fully aliphatic polymer. Another item to note is the edge clamping of the specimen as edge clamping for ballistics testing of laminates has been shown to result in greater resistance towards penetration (O’Masta et. al, 2015) as opposed to when specimens are clamed in other configurations.

With bulk material ballsitic testing the next step was to determine the effectiveness of the polymer as a matrix material for ballistic applications. The [0/90]s Kevlar/XDI-0 laminate produced to test H₃ was then subject to the same treatment as the XDI-0 film/disc samples using the same range setup. The following images show a new pellet alongside a deformed pellet after impacting the laminate and the deformed laminate following these ballistics tests. Four shots were fired
upon the laminate, only two deformed slugs were recovered due to the loss of the other two due to ricochet in unknown directions. Both recovered pellets were deformed in the same manner as shown in figure 59.

![Image of deformed pellets and laminate](image)

*Figure 59: Kevlar Ballistics, New Pellet, Deformed Pellet & Laminate*

No observable fiber failure or penetration was observed however the laminate was observed to deform around where impacts occurred. The deformed laminate showed signs of matrix cracking on the surface as shown in the following image.

![Image of laminate before and after treatment](image)

*Figure 60: [0/90]s Kevlar/XDI-0 before (Left) and after (Right) 1 hour 100°C treatment*

This laminate was then treated at 100°C for 1 hour at ambient pressure to promote matrix self-healing. When comparing the unhealed (Left) to the healed (right) laminate observable matrix cracks have been reduced. Although the laminate is deformed the lack of observable fiber failure and the ability to promote matrix self-healing is thought to be beneficial for ballistics.
applications. It is anticipated that future work will allow for ballistics testing with high velocity projectiles from firearms simulating ballistic protection under combat conditions with defense applications the focus of future research.

5.2.3 T-T\textsubscript{g} effective utility
The understanding of factors that influence healing efficiency is understood to be of utility with interest in autonomous and thermally accelerated self-healing of HUB based polymers. By understanding these relationships practical applications of these polymers designed around the understanding of ideal healing parameters. In this study a relationship between healing efficiency and healing temperature as a function of T-T\textsubscript{g} has been observed. Limitations of this study lie in the small sample sizes which do not allow for further statistical analysis and hypothesis testing to a high degree of confidence. Future work to forward the understanding of these relationships of time and temperature on healing efficiency will require the use of a redesigned tensile testing specimen and a greater sample size with time and temperature effects to be studied.
Acknowledgements

Having spent the last two years running between labs and periodically going to class between polymer syntheses I owe the following people and organizations my sincere thanks for their time, support, and direct efforts in supporting my research and my development as a scientist and engineer.

Dr. Lewis
Austin Bruce
Lucas Battisti
Delphi Technologies
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Society of Plastics Engineers

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Retrieved From:


Used for reference for recommended future tensile testing “dogbone” geometry given limitations using current specimen geometry.


Used for reference to fatigue life of composites and crack types in relation to inter and intralaminar cracking.


Used for formula to determine stress concentration factor for notched tensile specimens.


Composites Part A: Applied Science and Manufacturing, Elsevier

Retrieved From:

http://autonomic. beckman. illinois. edu/files/publications_papers/2003_Kessler_Composites.pdf

Used for reference of current self-healing composite systems currently proposed.
Retrieved From: http://sottosgroup.beckman.illinois.edu/nrs111.pdf
Used for an example of extrinsic self-healing methodologies for PMC laminate strength resoration.

Retrieved From: https://www.ncbi.nlm.nih.gov/pmc/articles/PMC2359850/
Used for refernce of current methodology of self-healing in PMC laminates in literature review.

Retrieved From: http://science.sciencemag.org/content/295/5560/1698/tab-figures-data
Used for example of current intrinsic self-healing/ Thermally mendable polymer.

Retrieved From: https://www.nature.com/articles/srep01093
Used for example of current development of self-healing polymers.

Retrieved From: https://arc.aiaa.org/doi/abs/10.2514/3.46904
Used as reference to discuss aeroelasticity as a concern for composite laminates in which matrix crack growth is of concern.

Retrieved From:


Used as reference material is discussion of delamination as problem in composite aerostructures as discussed in literature review.


Used for discussion of expected viscosity relationship & VFT.


Used as reference material for association, disassociation, and equilibrium constants for HUBs.


Retrieved From:

http://dx.doi.org/10.1016/j.ijimpeng.2015.08.012

Used as reference for penetration resistance of edge clamped laminates undergoing ballistics testing.
# Appendix:

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Grouping Information Using the Games-Howell Method and 95% Confidence

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Means that do not share a letter are significantly different.

Games-Howell Simultaneous Tests for Differences of Means

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Figure A1:XDI-0, Games-Howell
Games-Howell Pairwise Comparisons

Grouping Information Using the Games-Howell Method and 95% Confidence

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*Means that do not share a letter are significantly different.*

Games-Howell Simultaneous Tests for Differences of Means

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<th>Difference of Means</th>
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<th>Adjusted P-Value</th>
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Figure A2: XDI-25, Games-Howell

Games-Howell Pairwise Comparisons

Grouping Information Using the Games-Howell Method and 95% Confidence

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*Means that do not share a letter are significantly different.*

Games-Howell Simultaneous Tests for Differences of Means

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Figure A3: XDI-75, Games-Howell
Figure A4: Notch Geometry Detail Dwg.

Batch 76 Drying Study:

Figure A5: Batch 76 post-synthesis FTIR Results:
Figure A6: Batch 76T post-synthesis DSC Results:

Figure A7: Batch 76 post-cured 24hrs, 70°C DSC Results:
Figure A8: Batch 76 post-cured 48hrs, 70°C DSC Results:

Figure A9: Batch 76 post-cured 48hrs R2, 70°C DSC Results
Figure A10: Batch 76U post-cured 24hrs, 80°C DSC Results

Figure A11: Batch 76V post-cured 24hrs, 90°C DSC Results
Figure A12: Batch 78 post-cured 24hrs, 60°C DSC Results

Figure A13: Batch 78 post-cured 72hrs, 60°C DSC Results
### Statistics XDI-0 NEW B99,B90

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<td>225</td>
<td>638</td>
<td>5457</td>
<td>6029</td>
<td>6389</td>
<td>7059</td>
<td>7349</td>
</tr>
<tr>
<td>E-MOD(psi)</td>
<td>8</td>
<td>120539</td>
<td>5848</td>
<td>16542</td>
<td>100802</td>
<td>107502</td>
<td>115432</td>
<td>137228</td>
<td>146982</td>
</tr>
<tr>
<td>Energy(ft-lbf)</td>
<td>8</td>
<td>0.1863</td>
<td>0.0368</td>
<td>0.1042</td>
<td>0.0514</td>
<td>0.0889</td>
<td>0.1950</td>
<td>0.2673</td>
<td>0.3525</td>
</tr>
</tbody>
</table>

Figure A14: New Material Datasets, XDI-0,XDI-25,XDI-50,XDI-75
Figure A15: Batch 99 FTIR Report

Figure A16: XDI-0 Batch 101 Raw DSC Report
Figure A17: XDI-0 Batch 99 Post Cured DSC Report

Figure A18: XDI-25 Batch 100 Raw DSC Report
Figure A19: XDI-25 Batch 101 Post Cured DSC Report

Figure A20: XDI-75 Batch 84 Raw DSC Report
Figure A21: XDI-75 Batch 84 Post Cured DSC Report

Figure A22: XDI-75 Batch 91 Post Cured DSC Report
Figure A23: XDI-50 Batch 83 Raw DSC Report

Figure A24: XDI-50 Batch 83 Post Cured DSC Report
### Table: Healing Data

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Specimen</th>
<th>Tensile Strain at Fail (in/in):</th>
<th>Stress at failure (psi):</th>
<th>E-Modulus (psi):</th>
<th>Energy at Fail (ft-lbf):</th>
<th>% Recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td>12 Hours, 60°C</td>
<td>100A</td>
<td>4.542</td>
<td>820.550</td>
<td>168.070</td>
<td>0.728</td>
<td>2%</td>
</tr>
<tr>
<td></td>
<td>100B</td>
<td>3.492</td>
<td>770.140</td>
<td>507.416</td>
<td>0.651</td>
<td>11%</td>
</tr>
<tr>
<td></td>
<td>100C</td>
<td>5.132</td>
<td>808.600</td>
<td>272.800</td>
<td>0.806</td>
<td>27%</td>
</tr>
<tr>
<td></td>
<td>AVG:</td>
<td>4.692</td>
<td>799.763</td>
<td>316.095</td>
<td>0.729</td>
<td>13%</td>
</tr>
<tr>
<td>12 Hours, 70°C</td>
<td>100D</td>
<td>5.5113</td>
<td>1061.458</td>
<td>251.3560</td>
<td>1.0821</td>
<td>134%</td>
</tr>
<tr>
<td></td>
<td>100E</td>
<td>3.6555</td>
<td>788.295</td>
<td>528.4320</td>
<td>0.6012</td>
<td>10%</td>
</tr>
<tr>
<td></td>
<td>100F</td>
<td>5.8531</td>
<td>1047.270</td>
<td>226.4800</td>
<td>1.1077</td>
<td>154%</td>
</tr>
<tr>
<td></td>
<td>AVG:</td>
<td>5.0066</td>
<td>965.674</td>
<td>335.4227</td>
<td>0.9303</td>
<td>101%</td>
</tr>
<tr>
<td>12 Hours, 80°C</td>
<td>100G</td>
<td>4.575</td>
<td>857.710</td>
<td>304.141</td>
<td>0.759</td>
<td>156%</td>
</tr>
<tr>
<td></td>
<td>100H</td>
<td>5.210</td>
<td>815.440</td>
<td>236.554</td>
<td>0.777</td>
<td>212%</td>
</tr>
<tr>
<td></td>
<td>100I</td>
<td>3.903</td>
<td>726.647</td>
<td>336.275</td>
<td>0.616</td>
<td>159%</td>
</tr>
<tr>
<td></td>
<td>AVG:</td>
<td>4.563</td>
<td>799.999</td>
<td>292.323</td>
<td>0.717</td>
<td>175%</td>
</tr>
<tr>
<td>Room Temp</td>
<td>100J</td>
<td>4.908</td>
<td>859.039</td>
<td>280.687</td>
<td>0.863</td>
<td>20%</td>
</tr>
<tr>
<td>(48hrs)</td>
<td>AVG:</td>
<td>4.908</td>
<td>859.039</td>
<td>280.687</td>
<td>0.863</td>
<td>20%</td>
</tr>
</tbody>
</table>

### Figure A25: XDI-25 Healing Data Table

### Figure A26: XDI-25 T-Tg Curve
Figure A27: XDI-0 T-Tg Curve

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Figure A29: XDI-0 Healing Data Table, Batch 90

<table>
<thead>
<tr>
<th>Treatment:</th>
<th>SAMPLE:</th>
<th>INITIAL TESTING:</th>
<th>Healed Testing:</th>
<th>% Recovery:</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Tensile strain at Break (in/in)</td>
<td>Tensile stress at Break (psi)</td>
<td>Modulus (E-modulus) (psi)</td>
</tr>
<tr>
<td>32c 12 Hours</td>
<td>90A</td>
<td>5.54445</td>
<td>471.6762</td>
<td>187.4856</td>
</tr>
<tr>
<td></td>
<td>90B</td>
<td>6.51111</td>
<td>489.2843</td>
<td>160.0077</td>
</tr>
<tr>
<td></td>
<td>90C</td>
<td>5.16667</td>
<td>413.3421</td>
<td>189.5963</td>
</tr>
<tr>
<td>AVG:</td>
<td></td>
<td>5.7407433</td>
<td>458.1009</td>
<td>179.02989</td>
</tr>
<tr>
<td>60c 12 Hours</td>
<td>90D</td>
<td>6.58882</td>
<td>458.7472</td>
<td>148.19959</td>
</tr>
<tr>
<td></td>
<td>90E</td>
<td>10.87778</td>
<td>889.6789</td>
<td>104.31039</td>
</tr>
<tr>
<td></td>
<td>90F</td>
<td>4.84444</td>
<td>436.3269</td>
<td>210.31334</td>
</tr>
<tr>
<td>AVG:</td>
<td></td>
<td>7.4370133</td>
<td>534.7588</td>
<td>154.27444</td>
</tr>
<tr>
<td>Room Temp:</td>
<td>90G</td>
<td>7.14444</td>
<td>482.9104</td>
<td>140.82211</td>
</tr>
<tr>
<td></td>
<td>90H</td>
<td>5.1111</td>
<td>460.5057</td>
<td>187.45254</td>
</tr>
<tr>
<td></td>
<td>90I</td>
<td>4.24437</td>
<td>304.1982</td>
<td>154.57557</td>
</tr>
<tr>
<td>AVG:</td>
<td></td>
<td>5.49997</td>
<td>415.8714</td>
<td>160.95007</td>
</tr>
</tbody>
</table>

Figure A30: XDI-75 Batch 91 Initial Material Properties Data Table

<table>
<thead>
<tr>
<th>Specimen:</th>
<th>UTS (Ksi)</th>
<th>Strain at Failure (in/in):</th>
<th>Energy at tensile strength (ft-lbf):</th>
</tr>
</thead>
<tbody>
<tr>
<td>91A</td>
<td>6.362</td>
<td>0.159</td>
<td>0.24135</td>
</tr>
<tr>
<td>91B</td>
<td>7.349</td>
<td>0.184</td>
<td>0.35252</td>
</tr>
<tr>
<td>91C</td>
<td>7.007</td>
<td>0.173</td>
<td>0.27600</td>
</tr>
<tr>
<td>91D</td>
<td>5.457</td>
<td>0.098</td>
<td>0.08812</td>
</tr>
<tr>
<td>91E</td>
<td>6.051</td>
<td>0.097</td>
<td>0.09120</td>
</tr>
<tr>
<td>91F</td>
<td>7.076</td>
<td>0.148</td>
<td>0.18281</td>
</tr>
<tr>
<td>91G</td>
<td>6.021</td>
<td>0.146</td>
<td>0.20709</td>
</tr>
<tr>
<td>91J</td>
<td>6.416</td>
<td>0.086</td>
<td>0.05139</td>
</tr>
<tr>
<td>AVG:</td>
<td>6.467</td>
<td>0.136</td>
<td>0.18631</td>
</tr>
</tbody>
</table>

Figure A31: XDI-75 Batch 91 Healed Material Properties Data Table