THEMO-RESPONSIVE SELF-HEALING POLYMERS AND SELF-HEALING CARBON FIBER REINFORCED COMPOSITES

By

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To my family
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TABLE OF CONTENTS

ACKNOWLEDGMENTS .................................................................................................................. 4

LIST OF TABLES .......................................................................................................................... 8

LIST OF FIGURES ........................................................................................................................ 9

CHAPTER

1 INTRODUCTION ......................................................................................................................... 14

1.1 Motivation .............................................................................................................................. 15

1.2 Background ............................................................................................................................ 18

1.2.1 Self-Healing Mechanisms for Polymers ............................................................................ 18

1.2.1.1 Capsule Based .............................................................................................................. 21

1.2.1.2 Vascular ...................................................................................................................... 22

1.2.1.3 Intrinsic ....................................................................................................................... 23

1.2.2 Self-Healing Mechanisms for CFRP Composites ............................................................. 23

1.2.3 Diels-Alder Reaction ......................................................................................................... 27

1.2.4 Self-healing Polymer with DA Reaction .......................................................................... 29

1.2.5 Self-Healing Composites with DA reaction ..................................................................... 33

1.2.6 Shape Memory Polymer .................................................................................................. 37

1.3 Overview of Contributions .................................................................................................. 39

1.3.1 Application of the Shape Memory Recovery Force ......................................................... 39

1.3.2 Adaptable, Inexpensive Maleimide Moiety Synthesis ...................................................... 39

1.3.3 Directly Connected DA Healing Molecules ................................................................... 40

1.3.4 Bulk Specimens by Solvent-Free Polymerization Methods .......................................... 40

1.3.5 New Methods to Accurately Measure Transition Temperatures .................................... 41

1.3.6 Self-Healing Polymers with High Temperature Stability ................................................ 41

1.3.7 Self-Healing CFRP Composites with Healable Matrix ................................................ 41

2 SELF-HEALING POLYURETHANES WITH SHAPE RECOVERY .................................. 43

2.1 Chapter Introduction ............................................................................................................. 43

2.2 Polymer Syntheses .............................................................................................................. 46

2.2.1 Materials ........................................................................................................................ 46

2.2.2 4,10-Dioxatricyclo[5.2.1.02,6]dec-8-ene-3,5-dione (1) ..................................................... 46

2.2.3 4-(2-Hydroxy-ethyl)-10-oxa-4-aza-tricyclo[5.2.1.02,6]dec-8-ene-3,5-
dione (2) .................................................................................................................................. 47

2.2.4 N-(2-Hydroxyethyl)-maleimide (HEM) ............................................................................ 47

2.2.5 Pre-crosslinking DA Adducts (DA) ................................................................................ 48

2.2.6 Polymers .......................................................................................................................... 49

2.3 Characterization of the Diels-Alder Reaction ..................................................................... 50

2.3.1 Thermal Analysis of the Polymers ................................................................................. 50

2.3.2 Reversibility of the Self-Healing Mechanism ................................................................. 54
2.4 Characterization of Healing Performance of Polymers .............................................. 58
  2.4.1 Testing Method ........................................................................................................ 58
  2.4.2 Healing Process ........................................................................................................ 59
  2.4.3 Healing Performance ............................................................................................... 60
  2.4.4 Influence of Glass Transition Temperature and Molecular Mobility ....................... 63
  2.4.5 Shape Memory Characterization ............................................................................. 65
  2.4.6 Influence of Shape Memory Recovery Force .......................................................... 67
  2.4.7 Mechanical Properties ........................................................................................... 69
  2.5 Chapter Summary ....................................................................................................... 70

3 SELF-HEALING POLYMERS WITH HIGH TEMPERATURE STABILITY ........... 72
  3.1 Chapter Introduction ................................................................................................. 72
  3.2 Polymer Preparation .................................................................................................. 74
    3.2.1 Materials ............................................................................................................. 74
    3.2.2 HEM Synthesis .................................................................................................... 74
    3.2.3 Pre-Crosslinked Compounds (HTDA) Synthesis .................................................. 75
    3.2.4 Polymer Synthesis ............................................................................................... 76
  3.3 Characterization of DA reaction ............................................................................... 77
  3.4 Characterization of Healing Performance .................................................................. 79
    3.4.1 Healing Efficiency ............................................................................................... 79
    3.4.2 Thermal Analysis .................................................................................................. 83
    3.4.3 Mechanical Properties ......................................................................................... 85
  3.5 Chapter Summary ....................................................................................................... 87

4 CARBON FIBER REINFORCED POLYMER SELF-HEALING COMPOSITES ...... 88
  4.1 Chapter Introduction ................................................................................................. 88
  4.2 Composite Preparation ............................................................................................. 91
    4.2.1 Materials ............................................................................................................. 91
    4.2.2 Polymer Syntheses .............................................................................................. 91
    4.2.3 Composite Fabrication ...................................................................................... 93
  4.3 Characterization of Composite Healing Performance .................................................. 96
    4.3.1 Healing Process .................................................................................................... 96
    4.3.2 Healing Efficiency ............................................................................................... 97
  4.4 Chapter Summary ....................................................................................................... 102

5 CONCLUSIONS ............................................................................................................ 104
  5.1 Summary of Dissertation .......................................................................................... 105
  5.2 Contributions .......................................................................................................... 108
  5.3 Recommendations for Future Work ......................................................................... 109

APPENDIX: NUCLEAR MAGNETIC RESONANCE (NMR) SPECTRUMS ............ 112
  4,10-Dioxatricyclo[5.2.1.0.2,6]dec-8-ene-3,5-dione (1) .................................................. 112
  4-(2-Hydroxy-ethyl)-10-oxa-4-aza-tricyclo[5.2.1.0.2,6]dec-8-ene-3,5-dione (2) .......... 114
  N-(2-Hydroxyethyl)-maleimide (HEM) ....................................................................... 116
Pre-crosslinking DA Adducts (DA) ................................................................. 118
Pre-Crosslinked Compounds (HTDA) ............................................................ 120

LIST OF REFERENCES .................................................................................. 122

BIOGRAPHICAL SKETCH ............................................................................ 133
## LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-1</td>
<td>The average glass transition temperature, crosslinking temperature, and cleaving temperature and their standard deviations for 1DA1T, 1.5DA1T and 2DA1H.</td>
<td>53</td>
</tr>
<tr>
<td>2-2</td>
<td>The average healing efficiencies and standard deviations (SD) of the 1DA1T, 1.5DA1T, and 2DA1H polyurethane specimens.</td>
<td>61</td>
</tr>
<tr>
<td>2-3</td>
<td>The glass transition temperatures ($T_g$) of 1DA1T-0TDI and 1DA1T-0.5TDI.</td>
<td>64</td>
</tr>
<tr>
<td>2-4</td>
<td>The average healing efficiencies and standard deviations (SD) for three different 1.5DA1T specimen Types (A, B, and C).</td>
<td>69</td>
</tr>
<tr>
<td>2-5</td>
<td>Comparison of mechanical properties between 1DA1T, 1.5DA1T, 2DA1H, and epoxy.</td>
<td>70</td>
</tr>
<tr>
<td>3-1</td>
<td>The average healing efficiencies and standard deviations (SD) of the 0.5HTDA1T and 0.8HTDA1T polyurethane specimens.</td>
<td>82</td>
</tr>
<tr>
<td>3-2</td>
<td>Mechanical properties and standard deviations (SD) of 0.5HTDA1T and 0.8HTDA1T before and after heat treatment (compared to 1.5DA1T and epoxy).</td>
<td>86</td>
</tr>
<tr>
<td>4-1</td>
<td>The average healing efficiencies and standard deviations of C1.5DA1T, C2DA1H, and C0.8HTDA1T.</td>
<td>99</td>
</tr>
<tr>
<td>Figure</td>
<td>Description</td>
<td></td>
</tr>
<tr>
<td>--------</td>
<td>-------------</td>
<td></td>
</tr>
<tr>
<td>1-1</td>
<td>SEM image of mechanical damage in a CFRP composite after shear testing.</td>
<td></td>
</tr>
<tr>
<td>1-2</td>
<td>Schematic of chain interdiffusion in a thermoplastic polymer. Polymer temperature.</td>
<td></td>
</tr>
<tr>
<td>1-3</td>
<td>Schematic of healing agent delivery mechanism using polyethylene-co-methacrylic acid (EMAA) particles.</td>
<td></td>
</tr>
<tr>
<td>1-4</td>
<td>Three different healing systems.</td>
<td></td>
</tr>
<tr>
<td>1-5</td>
<td>Example of a capsule based self-healing FRP composite with various capsule area densities ((\rho)).</td>
<td></td>
</tr>
<tr>
<td>1-6</td>
<td>Example of a vascular self-healing FRP composite at varying magnifications.</td>
<td></td>
</tr>
<tr>
<td>1-7</td>
<td>A schematic of the healing process with thermoplastic additives (ethylene vinyl acetate, EVA) as a healing agent.</td>
<td></td>
</tr>
<tr>
<td>1-8</td>
<td>The Diels-Alder reaction mechanism.</td>
<td></td>
</tr>
<tr>
<td>1-9</td>
<td>Examples of dienes and dienophiles for the Diels–Alder reaction.</td>
<td></td>
</tr>
<tr>
<td>1-10</td>
<td>Multi-functional furan (4F) and maleimide (3M and 2MEP) moieties and the polymerization of 3M4F by using the DA reaction.</td>
<td></td>
</tr>
<tr>
<td>1-11</td>
<td>General presentation of polymeric diene bearing furfuryl functionality with bismaleimide as a dienophile.</td>
<td></td>
</tr>
<tr>
<td>1-12</td>
<td>X-ray micro-tomography images of a sample before and after heating.</td>
<td></td>
</tr>
<tr>
<td>1-13</td>
<td>Schematic of a maleimide functionalized glass fiber and a furan functionalized polymer network.</td>
<td></td>
</tr>
<tr>
<td>1-14</td>
<td>Chemical structures of A) poly(furfuryl alcohol), PFA and B) 1,1(^{-})-(Methylenedi-4,1-phenylene) bismaleimide, MDPB. Molecular structure of C) Epon 828 and D) EDR 176.</td>
<td></td>
</tr>
<tr>
<td>1-15</td>
<td>Molecular mechanism of the thermo-responsive shape memory effect.</td>
<td></td>
</tr>
<tr>
<td>2-1</td>
<td>Three steps synthesis of N-(2-hydroxyethyl) maleimide.</td>
<td></td>
</tr>
<tr>
<td>2-2</td>
<td>A schematic of the precrosslinked FA and HEM.</td>
<td></td>
</tr>
<tr>
<td>2-3</td>
<td>A schematic of the polymerization reaction with DA, TEA, and HDI monomers.</td>
<td></td>
</tr>
</tbody>
</table>
Representative TGA curves of 1DA1T, 1.5DA1T and 2DA1H. ........................................... 51
Representative differential scanning calorimetry data of 1DA1T, 1.5DA1T and 2DA1H. Crosslinking and cleaving transitions are marked. ........................................... 53
Proton VT NMR data for HEM and FA precrosslinked monomer to see the Diels-Alder reversibility ................................................................. 56
Carbon VT NMR of the DA monomer at two different temperatures to confirm the reversibility of the DA and rDA reactions. ........................................... 57
Dimension of a compact tension test specimen (unit in inches) with a thickness of 0.35” ................................................................. 58
Images of a specimen after cracking (left) and after the thermal healing process without the use of external forces (right). ........................................... 60
Maximum loads from the compact tension testing as a function of extensions after the first, second, and third healing cycles. ........................................... 61
Images of free strain recovery testings in two different directions for shape memory effect ................................................................. 66
Three different Types (A, B, and C) of CT test specimens with varying pre-crack lengths. ................................................................. 68
A schematic of the four steps required to synthesize HTDA monomer. ............... 76
A schematic of the polymerization process with HTDA, TEA, and HDI monomers. ......................................................................................... 77
VT $^1$H NMR spectra for the kinetics of the crosslinking DA reaction heating at 140 °C. ................................................................. 79
Representative load curves as a function of extension ........................................... 83
TGA and DSC curves for thermal stability ................................................................. 85
A schematic of the monomers’ (DA and HTDA) syntheses procedures. .............. 93
Schematic of vacuum assisted resin transfer molding system. ................................ 94
Short beam shear testing experimental setup. ................................................................. 97
Example SBS testing results for a specimen of C1.5DA1T, C2DA1H, and C0.8HTDA1 for the first, and second healing. ................................................................. 98
Optical microscopy images of a composite laminate specimen before and after healing................................................................. 99
4-6 SEM images of C0.8HTDA1T showing four different damages from SBS testing

A-1 A proton NMR spectrum for product 1

A-2 A carbon NMR spectrum for product 1

A-3 A proton NMR spectrum for product 2

A-4 A carbon NMR spectrum for product 2

A-5 A proton NMR spectrum for HEM

A-6 A carbon NMR spectrum for HEM

A-7 A proton NMR spectrum for DA

A-8 A carbon NMR spectrum for DA

A-9 A proton NMR spectrum for HTDA

A-10 A carbon NMR spectrum for HTDA
The development of self-healing materials has grown over the past decade due to their ability to repeatedly repair damage that has occurred before complete material failure. In this work, polymers that can be intrinsically healed through thermal stimulation are first investigated, followed by self-healing carbon fiber reinforced polymer (CFRP) composites which are fabricated by embedding the healable polymers as the matrix.

In the existing literature for thermo-responsive self-healing polymers with an intrinsic system, the Diels-Alder (DA) reaction is one of the most promising mechanisms since it is highly efficient, simple, and is repeatable with only the application of heat. However, the limitations of current self-healing polymers include the required use of an external force to close crack surfaces and the relatively low cleaving temperature (~120 °C) for the reverse reaction, which can limit such materials in high performance applications.

To overcome these challenges, two new approaches with regards to the DA reaction are developed. First, by using maleimide and furan moieties as the DA healing
agents, new thermo-responsive self-healing polymers are developed that use the force from the shape memory effect to close two crack surfaces instead of external forces. Secondly, by introducing maleimide and anthracene DA moieties, self-healing polymers with increased cleaving reaction temperature above 250 °C are developed. This work represents the first demonstration of a polymer network acquiring large and repeatable healing behavior only through the crosslinking DA reaction. In addition, this work is the first to show verification of the healing performance through mechanical testing on bulk specimens that exhibit a high use temperature. In general, the polyurethane polymers developed show stable structure and superior and repeatable healing performance with mechanical properties comparable to commercial epoxies. It is further shown that the self-healable polyurethanes can be used to fabricate CFRP with repeatable healing and comparable properties to engineered materials.
CHAPTER 1
INTRODUCTION

There has been an increased focus on developing self-healing materials since all materials have the potential to become damaged or degraded over time by various mechanical, chemical, thermal and UV radiation factors\textsuperscript{1,2}. The self-healing ability is especially appealing for polymers and composite materials since these types of materials are often used in large-scale applications and it would be beneficial to be able to repair damaged areas in situ. For example, if an aircraft part made of fiber reinforced polymer (FRP) composites were to become damaged, a healing mechanism such as heat could potentially be employed to heal the damage without removing the part, thus allowing the aircraft to resume operations much faster. Self-healing materials could also be useful in space where the environment adversely affects repair operations. Moreover, self-healing polymers could potentially be used in everyday applications, such as a coating material to protect electronic products (e.g., cell phones and laptops) and automobile parts from minor damages. By incorporating self-healing materials, the life and cost efficiency of products and components can increase\textsuperscript{3}.

Therefore, innovative thermally responsive self-healing polymers were developed that use the shape memory effect to eliminate the use of external forces (e.g., clamps) during the healing process. Additional novel self-healing polymers with high temperature stability were studied and their healing performances as well as durability were examined. Moreover, carbon fiber reinforced polymer (CFRP) composites were fabricated by using the developed self-healing polymers as the matrix in the composites. A large part of this process was the proper characterization of the new polymer, and this research has contributed greatly to the current body of knowledge concerning not only
self-healing and shape memory polymers, but also CFRP composites. A further
discussion on current literature can be seen in the following sections.

1.1 Motivation

CFRP composites are considered as an excellent replacement material for metal
and wood due to its specific strength and stiffness\textsuperscript{4}. This is evident when considering
the various applications where CFRP composites have been employed, including
automobiles, aircrafts, sporting goods, and protection gears\textsuperscript{5-10}. However, for CFRP
composites, long-term stability has always been an issue\textsuperscript{11-13} since mechanical damage
can occur after repeatable usage\textsuperscript{14,15}. An example of such damage can be seen in
Figure 1-1. As a result, much research has targeted improving the life and durability of
composites, and self-healing FRP composites are a promising solution.

![SEM image of mechanical damage in a CFRP composite after shear testing.][1]

Therefore, research is conducted with the ultimate goal of fabricating intrinsically healable FRP composites in mind. The first part of this work focuses on the synthesis of an intrinsically healable polymer matrix that can be used during the CFRP composite fabrication process. The use of an intrinsic mechanism is prioritized over either a capsule based or vascular system, and the use of a healable matrix is chosen over other intrinsic healing methods such as healing molecules grafted on the fiber. For the former method, separate media which contains healing agents can eventually act as defects after the healing process. Moreover, the latter method is often conducted for fiber surface functionalization grafting reversible molecules to achieve the healing property on the interfacial area between matrix and fiber reinforcements. However, a high degree of fiber treatment to increase the concentration of reversible molecules on the fiber surface can damage the fiber and eventually lower the strength of reinforcements, which may affect the strength of the whole composite. For these reasons, an inherently healable polymer matrix is extensively studied rather than the other mechanisms due to the potential application of self-healing polymers as not only the matrix in FRP composites but also as coating materials on electronic devices or automobile exteriors.

Self-healing polymers have been inspired by biological systems which can respond to damage autonomously, and a number of self-healing polymers have been developed over the last decades. So far, the DA reaction has been shown to be the most promising in regards to the development of high modulus thermo-responsive self-healing polymers. This is because the DA reaction is an intrinsic mechanism meaning that healing performance can be undergone without additional healing agents in the
polymer network. Self-healing polymers that include the DA reaction are highly efficient and simple and can be repeatedly healed through only the application of heat. Therefore, self-healing polymers with the DA reaction were investigated in this research and CFRP composites with the self-healing DA matrix were fabricated.

When considering the self-healing polymers synthesized with the DA reaction in the literature, there are still some limitations that have driven the focus of this research. First, external forces are needed to make two crack surfaces close to one another. This means that more than one external stimulus is required. Second, the stability and mechanical properties of these self-healing polymers are not comparable to commercial epoxy. For instance, the first DA polymers reported by Chen et al. are not very stable since only the DA intermolecular bonds are an interlinkage in the polymers\textsuperscript{16,17}. These bonds can be completely cleaved by heating them above 120 °C for an extended period of time. Other types of DA polymers have been developed by embedding free healing agents in the polymer network without actually connecting these agents to the main chain. This approach can cause the polymers to have varying and unpredictable properties that are dependent on the amount of free agent in the polymers. Lastly, due to costs associated with DA monomers, synthesis of DA self-healing polymers for industrial applications is a concern.

After considering these imitations, new thermo-responsive self-healing polyurethanes with shape memory effects are developed so that no external forces are required to heal cracks. The polymers exhibit high stability and the improved mechanical properties can be attributed to the fact that all the DA monomers are connected to the polyurethane’s main chain. Also, the design of an inexpensive and
high yield maleimide monomer synthesis method (dienophile molecule) is studied to produce high quality monomers. This could have the potential to be used in the scaled up synthesis of self-healing polymers for industrial applications.

1.2 Background

1.2.1 Self-Healing Mechanisms for Polymers

There are several different types of polymer self-healing mechanisms that have been developed mostly for thermoset polymers over the last couple of decades. This is because thermoplastic polymers can be healed by simply melting and filling in the damaged areas. However, when the self-healing concept was introduced in the 1980s, the first type of healing mechanism involved only thermoplastic polymers that were able to be healed via molecular interdiffusion\textsuperscript{18-21}. This general mechanism involves chain interpenetration across the interfaces as shown in Figure 1-2. Figure shows the schematics of chain interdiffusion in a thermoplastic polymer at three different polymer temperatures (below the T\textsubscript{g}, at the T\textsubscript{g}, and above the T\textsubscript{g}). As shown, a limitation of this mechanism is that the interactions between crack surfaces below the glass transition temperature (T\textsubscript{g}) are not sufficient. Thus, only above the T\textsubscript{g}, the chain segments start to diffuse effectively to the crack surfaces and create physical crosslinks\textsuperscript{22,23}. To increase the chain mobility with minimal heat, the T\textsubscript{g} of polymers could be lowered and therefore, methanol induced by Lin et al.\textsuperscript{24} and ethanol induced by Wang et al.\textsuperscript{25} crack healing methods in poly(methyl methacrylate) were investigated. As a result, the T\textsubscript{g} was decreased due to the plasticization effect, and chain diffusion was promoted across the surfaces.
Figure 1-2. Schematic of chain interdiffusion in a thermoplastic polymer. Polymer temperature A) below the $T_g$, B) at the $T_g$, and C) above the $T_g$. [Reprinted with permission from Jud, K. & Kausch, H. Load transfer through chain molecules after interpenetration at interfaces. *Polym. Bull.* 1, 697-707 (1979)]

More recently, blends of thermoset and thermoplastic polymers have been developed, as shown in Figure 1-3, where the thermoplastic polymers act as healing agents above the melting temperature$^{2,26-28}$. Due to the meltable thermoplastic healing agents, the stability of the polymer dramatically deceases above the melting point of the thermoplastic agent. Moreover, the potential for phase separation between the thermoset and thermoplastic polymers might cause poor interfacial strength. Also, unexpected reactions might occur and produce by-products such as gases. However, this system still contains various advantages such as an inexpensive process method, an easy synthesis method, high healing efficiency and repeatability$^{29,30}$. As a result, extensive research on this system has been conducted in order to improve the drawbacks and optimize the ratio of thermoset to thermoplastic polymers to ensure
good compatibility, while maintaining polymer strength and repeatable healing performance\textsuperscript{29}. Researchers have incorporated blends of thermoset and thermoplastics polymers as the matrix for FPR composites, since these mendable resins can easily fill delamination through the application of heat\textsuperscript{31-34}.

![Figure 1-3. Schematic of healing agent delivery mechanism using polyethylene-co-methacrylic acid (EMAA) particles\textsuperscript{272727}. [Reprinted with permission from Meure, S., Wu, D. Y. & Furman, S. Polyethylene-co-methacrylic acid healing agents for mendable epoxy resins. Acta Mater. 57, 4312-4320, (2009)]]

For thermoset polymers, there are three main different types of healing mechanisms: (1) capsule based, (2) vascular, and (3) intrinsic as shown in Figure 1-4\textsuperscript{3}. Generally, capsule and vascular based healing systems are considered extrinsic systems since they store healing agents in different media that has been embedded into the polymer matrix. Meanwhile, intrinsic systems contain the healing functionality in their matrix and can be healed multiple times. The advantage of an extrinsic system is that
healing can be triggered once cracks are induced, but unlike an intrinsic system, the mechanical properties of the healed polymers could be different after integration of the healing agents\textsuperscript{35}. Also, for bulk application, the multiple reagents in the separate media could be expensive and difficult to fabricate\textsuperscript{30}.

![Figure 1-4. Three different healing systems. (Reprinted with permission from Blaiszik, B. et al. Self-healing polymers and composites. *Annu. Rev. Mater. Res.* \textbf{40}, 179-211 (2010))](image)

1.2.1.1 Capsule Based

For thermoset polymers, the most studied healing system in recent years is one which contains embedded healing agents microcapsules\textsuperscript{2,12,36-38}. The healing process is triggered when a crack ruptures the capsules and the healing agent is released into the damaged area by capillary forces\textsuperscript{39}. There are typically two materials required in this system; the healing agent and a polymerizer that reacts with the healing agent to solidify the region\textsuperscript{35}. There are numerous ways in which the healing agents and polymerizers can be stored and then dispersed in the matrix. In general, healing agents are stored in capsules and polymerizers are located in the matrix, in other capsules, or as a separate phase. The most well-known self-healing system using microcapsules seen in the literature is the ring-opening metathesis polymerization (ROMP) in dicyclopentadiene (DCPD) with Grubb’s catalyst\textsuperscript{12,40-43}. The advantage of this system is
that the healing can be autonomously initiated once a crack is induced and the capsules are ruptured. However, one of the biggest disadvantages is that the same spot cannot be healed multiple times once the healing agent supply has been exhausted.

1.2.1.2 Vascular

The next healing system involves the use of vascular tubes inside the polymer matrix. The healing agents can be refilled through the tubes after depletion for repeatable healing performance and therefore the main strength of this system is to allow for the continuous and autonomous healing of damages. Similar to the capsule based system, various methods to separate and disperse the healing agents and polymerizers have been developed. For instance, they both can be stored in different tubes, or polymerizers can be dispersed in the matrix with healing agents in vascular tubes. Three different types of vascular networks include those that are one-dimensional (1D), two-dimensional (2D), and three-dimensional (3D). The simplest technique for a 1D network is to use hollow glass fibers to introduce the healing agents and polymerizers since glass fibers have very good compatibility with many healing agents and polymerizers\textsuperscript{44-47}. 2D and 3D techniques have interconnected points that can improve the reliability from channel blockages\textsuperscript{48-50}. These networks try to mimic the blood vessel systems of human skin that trigger blood flow to create a scab on a wound area when the skin is cut\textsuperscript{51}. However, some drawbacks to this system are that if the same area on a tube is ruptured multiple times, the potential exists for the tube to stop functioning and delivering healing agents. Also, the empty tubes can act as another type of defect in the matrix. Such drawbacks can eventually reduce the properties of the polymer and reduce healing performance.
1.2.1.3 Intrinsic

The last healing system is an intrinsic system that can partially or fully repair the original properties of a polymer multiple times without any other remaining additional defects after the healing process. This system can be less complex than the extrinsic systems since variables such as compatibility between healing agents and capsules/tubes, and integration of them, can be neglected in this system\(^3\). Moreover, defects do not remain after multiple healing cycles although an external stimulus needs to be applied to trigger the healing process. This has resulted in much research being conducted on this system in recent years. Therefore, with this research, the intrinsic healing mechanism by using reversible reactions (i.e., Diels-Alder (DA) reaction\(^{17,52,53}\), hydrogen bonds\(^{54-56}\), and boronic ester cross-links\(^{57,58}\) etc.) was studied and employed due to the ability to encourage a repeatable healing process with uniform properties. Among all the healing mechanisms, the thermally reversible DA reaction was utilized in this research. More detailed information on the DA reaction as a healing mechanism are discussed in Section 1.2.3. Diels-Alder Reaction and Section 1.2.4. Self-healing Polymer with DA Reaction.

1.2.2 Self-Healing Mechanisms for CFRP Composites

There are several types of self-healing mechanisms for composites and in general these systems are similar to those of self-healing polymers. For example, a healing agent can be included in capsule shells and then embed between the reinforced fibers\(^{59}\). In CFRP composites, the most common defect involves delamination of the fibers, meaning that the polymer matrix would also be heavily damaged. Therefore, as shown in Figure 1-5, healing agent microcapsules located in the polymer are attached
to the fiber surfaces during the composite fabrication process. Then, healing can be performed autonomously once damages are induced and the capsule shells are broken.

Figure 1-5. Example of a capsule based self-healing FRP composite with various capsule area densities ($\rho$). 59 59 59 [Reprinted with permission from Blaiszik, B. J., Baginska, M., White, S. R. & Sottos, N. R. Autonomic Recovery of Fiber/Matrix Interfacial Bond Strength in a Model Composite. Adv. Funct. Mater. 20, 3547-3554, (2010)]

Similarly, a vascular system of the 2D and 3D networks is also possible in FRP composites11,60-62. In this system, hollow vascular tubes containing healing agent are placed between fiber stacks and the healing agents are released when any damages rupture the tubes. In Figure 1-6, the larger dark circles are examples of vascular tubes
with healing agent between the carbon reinforced fibers. For both microcapsules and vascular systems, the fundamental concepts are the same as those for the polymers, but an additional phase (fiber reinforcement) is added to the composites.

Figure 1-6. Example of a vascular self-healing FRP composite at varying magnifications. The scale bars indicate A) 1 mm, B) 0.1 mm, and C) 0.1 mm. [Reprinted with permission from Williams, G., Trask, R. & Bond, I. A self-healing carbon fibre reinforced polymer for aerospace applications. *Composites Part A.* **38**, 1525-1532 (2007)]

For the intrinsic healing system in the FRP composites, one possible method is to disperse a separate polymer phase as a healing agent in the matrix. If needed, heat can be applied to the composite in order to melt the discrete phase, which then migrates to the crack. For instance, Zako and Tokano employed 40% by volume uncured epoxy particles in a glass fiber reinforced polymer (GFRP) composite. With the application of heat at 120 °C for 10 minutes, 100% stiffness from a three-point bending testing was recovered. Similarly, another type of intrinsically healable matrix in FRP composites was developed by blending two phases (thermoplastic and thermoset) into the FRP composites, where the thermoplastic phase acted as a healing agent. As shown in Figure 1-7, when heat was applied, the thermoplastic polymer melted and filled the damages, and as a result a 50-70% healing recovery was achieved by Hayes et al. and a 57-156% healing was achieved by Pingkarawat et al. Interestingly, in the work by Pingkarawat et al., a healing efficiency greater than 100%
was obtained in one of the self-healing CFRP composite specimen when the thermoplastic healing agent increased the adhesion on the carbon fiber surface after healing. However, the biggest drawback to this type of system where the healing agent in the form of an uncured epoxy or thermoplastic is mixed into the matrix is that discrete unstable phases can affect the mechanical properties and stability of the final product. This can be due to poor interfacial adhesion or the occurrence of an unwanted reaction between the two separate phases. Moreover, applications are limited to temperatures below the thermoplastic’s melting point, thus restricting the temperature range for which the composite can be used. Finally, intrinsically healable molecules using a reversible reaction (such as the DA reaction) can be embedded into the polymer matrix via three different methods that will be further discussed in Section 1.2.5.

Self-Healing Composites with DA Reaction.

1.2.3 Diels-Alder Reaction

The Diels-Alder (DA) reaction is a thermally reversible reaction between a conjugated diene and a dienophile, from which the resultant product is a cyclohexene derivative. The DA adducts after crosslinking, but can still undergo a reverse reaction at higher temperatures which is known as a retro Diels-Alder (rDA) reaction. The DA reaction is known as a concerted reaction, which means the breaking and creation of bonds occurs in a single step. Four electrons from the conjugated diene and two electrons from the dienophile are involved so it is also called a [4+2] cycloaddition reaction. Essentially, three π bonds break and two new C-C σ bonds and one new C-C π bond are formed as shown in Figure 1-8.

Figure 1-8. The Diels-Alder reaction mechanism.

Among all of the dienes and dienophiles presented in Figure 1-9, the furan and maleimide groups have been the most commonly selected for use in the synthesis of self-healing polymers. This is because the only limitation of the diene used in the DA reaction is for it to be s-cis conformation (the double bonds are cis about the single bond, s= single); however, the cis conformation is thermodynamically less stable due to steric repulsion, especially when the substituents are larger than hydrogen. Thus, the furan group is a very reactive diene since the cis conformation is already locked in its structure. However, the furan group might be too reactive and the rDA reaction
temperature is relatively low (approximately 120 °C). Therefore, as a diene, the anthracene group has been studied and in theory, the cleaving temperature can increase to 250 °C. Similar to the furan group, the conformation is locked in the cis position and therefore, the anthracene group is also an appropriate candidate for the diene. For a dienophile monomer, maleimide groups are typically chosen. In order to increase the reactivity of the dienophile, it is necessary to have one or more electron-withdrawing groups, such as a carbonyl group (C=O) or a cyano group (C≡N), attached to the C=C bond. The role of electron-withdrawing groups are to withdraw electrons from the C=C bond and to make the sp2 carbon have a partially positive charge. This partially positive charge helps the dienophile be more reactive toward the diene groups. Therefore, maleimide moieties with two C=O bonds can be a good dienophile candidate.

![Figure 1-9. Examples of dienes and dienophiles for the Diels–Alder reaction.](image)

1.2.4 Self-healing Polymer with DA Reaction

Diels and Alder first introduced their chemical cycloaddition in 1928. After approximately 40 years, the DA reaction between furan and maleimide molecules among all possible dienes and dienophiles was illustrated for the first time in 1969 by Craven et al. Then, it took more than 30 years for Chen et al. to publish work on thermally remendable self-healing polymers by using the reversible DA reaction in 2002 and 2003.

There are many advantages to using the DA reaction to create self-healing polymers. First, the path of a crack can be controlled, since the new σ bond of the DA adduct has a much lower bond energy than other covalent bonds. In detail, Chen et al. determined with a differential scanning calorimeter that the bond energy of the DA adducts is 96.2 kJ/mol. Also, Konovalov and Kiselev reported that the C-C bond energy between anthracene and maleimide are from 77 kJ/mol to 117 kJ/mol depending on the attached substituents. For comparison, other covalent bond energies are 348 kJ/mol for C-C bonding, 293 kJ/mol for C-N bonding, and 389 kJ/mol for N-H bonding. This implies that covalent bonds are at least 2 to 3 times stronger than the intermolecular bond between the DA adducts. Therefore, cracks are more likely to propagate through new C-C σ bonds over other bonds. Due to this, once the broken bonds are reformed, healing is possible on the crack surfaces in principle and therefore, the healing efficiencies directly refer to the recovery of broken DA crosslinks. This was a vital finding that showed how DA reactions could be used for self-healing polymers. Second, the DA reaction occurs slowly at room temperature without any other external stimulus and the reaction becomes faster as the temperature increases. Thus, DA polymers can still prevent the propagation of micro-damage at room temperature. Third, the
temperatures for the rDA reaction (120 °C between furan and maleimide\textsuperscript{16,17} and 250 °C between anthracene and maleimide\textsuperscript{78,80}) are low enough for thermal degradation and also high enough for applications\textsuperscript{85}. For all of these reasons, the DA reaction has been studied to develop thermo-responsive self-healing polymers.

As previously mentioned, Chen et al. was the first to report on the development of self-healing polymers through the DA reaction with multi-furan and multi-maleimide groups\textsuperscript{16,17,82}. Their first monomers contained four furan moieties (4F) and three maleimide moieties (3M) on each molecule as shown in Figure 1-10. This polymer was formed via the DA reaction of furan and maleimide monomers. The average healing efficiency of this 3M4F polymer was approximately 50% at 150 °C and 41 % at 120 °C\textsuperscript{17}. Chen et al. then improved the efficiency to around 80 % at 115 °C by using a low melting point maleimide monomer (2MEP) as shown in Figure 1-10. This monomer allowed for a higher mobility of molecules, resulting in a better ability to heal cracks more effectively\textsuperscript{16}. With the low melting point monomer, the average healing efficiency improved by roughly 30 % compared to Chen et al.’s original work. In other words, the mobility of the molecules was shown to be an important factor that can potentially have a significant effect on the healing efficiency.

After the publications by Chen et al., a number of other researchers have reported on the 2MEP4F polymer. Plaisted et al. evaluated the 2MEP4F polymer developed by Chen et al. more quantitatively\textsuperscript{86}. Ghezzo et al.\textsuperscript{87,88} and Part et al.\textsuperscript{52} prepared self-healing composites with the polymer developed by Chen et al. and carbon fiber.

Unlike the polymers synthesized by Chen et al. with the DA reaction, there has been more research by Gheneim et al. on the synthesis of polymeric dienes; bearing pendant furan moieties to the main chain in a polymer, whereas the maleimide moieties are embedded as a crosslinking agent or vice versa. Similarly, Amalin Kavitha and Singha investigated a polymethacrylate bearing furfuryl functionality with bismaleimide as shown in Figure 1-11. Also, Zhang et al. and Toncelli et al. developed the furan functionalized thermosetting polyketones with bismaleimide as a crosslinking agent. Healing is possible in this system since the free healing agents become crosslinked with the other bearing moieties. The primary benefit of having free maleimide or furan moieties is that these molecules have increased mobility and are better able to find the pair moieties when healing is initiated.

However, there are still some disadvantages and limitations to using the DA reaction. First, the polymers might not be stable as a complete polymer since currently developed polymers have been synthesized by either crosslinking only the DA monomers to form networks\textsuperscript{16,17,82} or embedding free crosslinking agents in the polymers\textsuperscript{89-92}. The former polymers can be completely cleaved by heating them above 130 °C (the cleaving temperature) since the only interlinkage in these polymers is the DA intermolecular bonds, and the latter polymers can have varying properties depending on the amount of free agents in the polymers. Moreover, it is currently expensive to synthesize the DA monomers. This could potentially hinder large scale production of DA self-healing polymers for industrial applications.

To overcome the low stability of polymers, the polymers in this research were designed to have the healing molecules directly grafted to the main chain in the polymer structure. Accordingly, a polyurethane network was chosen since it provides a stable
structure with advantageous mechanical properties for a variety of applications. Furthermore, the dienophile monomers synthesized in this research was inexpensive and could help to alleviate the current limitation associated with trying to scale up self-healing polymer production for industrial applications.

1.2.5 Self-Healing Composites with DA reaction

After Chen et al. developed their self-healing polymers with the DA reaction, further research related to self-healing FRP composites has been conducted, especially with the use of their developed molecules known as 4F, 3M, and 2MEP which are shown in Figure 1-10. By using these molecules, Park et al. and Ghezzo et al. tried to fabricate self-healing CFRP composites\textsuperscript{52,70,87,88}. The self-healing CFRP composites were produced using a resin transfer mold (RTM) method after all the monomers were mixed at the melting temperature. Then, the healing performance was evaluated based on the tensile strain values and, as a result, around 90% of the tensile strain was recovered. Figure 1-12 shows the x-ray micro-tomography images of the CFRP composites before and after the healing process\textsuperscript{52}. The novel method of this work was their use of electrical resistive heating to increase the temperature of the CFPR composites during multiple healing procedures.

![X-ray micro-tomography images of a sample before and after heating.](image)

Figure 1-12. X-ray micro-tomography images of a sample before and after heating. [Reprinted with permission from Park, J. S. \textit{et al.} Multiple healing effect of thermally activated self-healing composites based on Diels–Alder reaction. \textit{Compos. Sci. Technol.} \textbf{70}, 2154-2159, (2010)]
Further research has been conducted to increase the adhesion between the polymer matrix and fiber reinforcements since interface interaction affects the properties of composites by controlling the load transfer between the matrix and fibers\textsuperscript{93,94}. As shown in Figure 1-13, Peterson et al. demonstrated functionalization methods on the surface of glass fibers with maleimide and of an epoxy-amine thermosetting matrix with furan\textsuperscript{93}. The GFRP composites were fabricated using functionalized fibers and a matrix, and the healing performance was characterized via short beam shear (SBS) testing. In the work by Peterson et al., a relatively low average healing efficiency of 41\% was obtained. Therefore, in order to increase the healing efficiency while maintaining good interface strength, Gong tried to use 2MEP4F as the matrix with maleimide functionalized glass fibers\textsuperscript{94}. The results suggested that the interfacial strength between the functionalized glass fibers and the 2MEP2F polymer matrix was considerably improved by up to 20\%. Gong did not determine the healing ability of this composite, but it is believed that the healing efficiency should be better than the non-functionalized CFRP composite fabricated by Part et al. using 2MEP4F.

The CFRP composites fabricated with 2MEP4F provided good healing performance and the surface functionalized GFRP composites fabricated with either furan functionalized epoxy or 2MEP4F demonstrated both an improved interfacial strength between the fibers and matrix, as well as improved healing performance. However, there are some drawbacks to these composites, including that the chemical synthesis process is relatively complicated\textsuperscript{95,96} and that the strength of the matrix is not as good as some commercial epoxy resins. Also, to obtain good healing performance, a high degree of fiber treatment was required in order to functionalize a sufficient amount
of healing agent on the fiber surfaces. By doing so, fibers could be greatly damaged and this might be a reason why carbon fiber functionalization has not been conducted to fabricate self-healing CFRP composites.

Therefore, additional research has been performed to improve these drawbacks\textsuperscript{94}. As shown in Figure 1-14, a blend of commercially available remendable resin, poly furfuryl alcohol (PFA) and 1,1\textsuperscript{-}(Methylenedi-4,1-phenylene) bismaleimide (MDPB), and epoxy with diglycidyl ether of bisphenol A (DGEBA) and EDR 176 hardener was developed. All of these resins are commercially available and three different specimens with three different ratios were prepared in order to optimize the right ratio for healing. For the sample preparation, all the monomers were mixed well at room temperature and then the mixed resin was poured on top of unidirectional carbon.
After, the polymer composites were cured at 115 °C for 15 hours. Therefore, the synthesis process was much more simplified when compared to the composites with 2MEP4F. Healing was confirmed by SBS testing and, depending on the amount of healable resins, healing efficiency ranged from 80-120% for the first healing cycle and 67-107% for the second healing cycle. In order to compare the mechanical properties of the developed polymer composites to the ones fabricated with epoxy and 2MEP4F, the SBS strength was measured. The SBS strengths of all three of Gong’s composites were higher than the composites fabricated with 2MEP4F and one of Gong’s composites was comparable to the composite created with epoxy. However, the composite with the lowest healing efficiency exhibited the highest SBS strength, while the other composite with the highest healing efficiency exhibited the lowest SBS strength, similar strength to the one with 2MEP4F. These results indicate that even though the strength of Gong’s composites increased, the healing performance did not. Hence, further research is recommended to simultaneously increase both composite healing and strength.

Figure 1-14. Chemical structures of A) poly(furfuryl alcohol), PFA and B) 1,1’-(Methylenedi-4,1-phenylene) bismaleimide, MDPB. Molecular structure of C) Epon 828 and D) EDR 176. [Adapted from Gong, C. Synthesizing Smart Polymeric and Composite Materials 3563455 thesis, University of California, Los Angeles, (2013)]
1.2.6 Shape Memory Polymer

A shape memory polymer (SMP) is a newer polymer group that has the capability of memorizing its permanent shape, even if it is temporarily distorted by an external stimulus. They are capable of changing their shapes upon the application of an external stimulus\(^97\), and this phenomenon is known as the shape memory effect. Within SMPs, there are several types that can be classified depending on the way they react to stimulus. They include thermally (thermo-responsive) induced, electrical current or voltage induced (electro-responsive), chemically induced (chemo-responsive), or light induced (photo-responsive) shape memory polymers\(^98\). However for this research, thermo-responsive shape memory polymers are the main focus.

An advantage of SMPs is their versatility since they can be synthesized to have a wide range of properties depending on their chemical structures and compositions\(^99\). According to Lendlein et al., the shape memory effect arises from the combination of the structure and morphology of a polymer. In SMPs, two notable features exist, a soft segment (switching segment) and a hard segment (netpoint)\(^100\). The temporary shape of an SMP is memorized in a soft segment (switching segment) that consists of the chain in domains, while the permanent shape is remembered in a hard segment (netpoint) that can consist of covalent bonds or intermolecular interactions\(^97,100,101\). Moreover, there are two transition temperatures; a hard segment deforms above the highest transition temperature (\(T_{\text{perm}}\)), whereas a soft segment becomes flexible above the second thermal transition temperature (\(T_{\text{trans}}\)).

Figure 1-15 is a schematic representation of how the shape memory effect works. A polymer with a permanent shape must first be synthesized then the polymer is deformed by external stress at a temperature above \(T_{\text{trans}}\). This is followed by a period
where the polymer is cooled down to room temperature to fix the temporary shape. When heat is then applied to the polymer above $T_{\text{trans}}$, but below $T_{\text{perm}}$, the temporary shape of the polymer returns to its permanent shape.

![Figure 1-15. Molecular mechanism of the thermo-responsive shape memory effect.][1]


Wilson et al. developed a shape memory polyurethane by using monomers with highly symmetrical molecules, such as hexamethylene diisocyanate (HDI), triethanolamine (TEA), and N,N,N',N'-tetrakis(hydroxypropyl)ethylenediamine (HPED), to form an amorphous polymer network$^{101}$. These authors were able to validate that the ideal elastomer behavior of their polymer occurred above the glass transition temperature ($T_g$). Garcia et al. was able to successfully demonstrate a novel autonomous materials system using a fiber optic network on Wilson et al.’s shape memory polymers$^{102}$. This result is important since it shows the potential of SMPs in an autonomous materials system.

In this research, the polyurethane developed by Wilson et al. was modified by adding reversible molecules to synthesize new polymers with shape memory effects.
Therefore, the use of external forces would not be required for the polymer to return to its original shape. Also, the only external stimulus needed to initiate the healing process would be heat. Requiring only the use of one stimulus such as heat can be an important factor for future work involving the design of autonomous polymer network systems.

1.3 Overview of Contributions

This following sections present an overview of the contributions made by this research to the development of self-healing materials. Several novel methods were used to develop self-healing polymers and CFRP composites.

1.3.1 Application of the Shape Memory Recovery Force

The first meaningful contribution of this research is the introduction of the use of the shape memory recovery force to reduce the number of external stimuli in an intrinsic healing system. External pressure has been a critical requirement in order to get the crack surface in adjacent contact before initiating the healing process. This research represents the first time that one phase polymers have been synthesized combining self-healing and shape memory functionalities. The integration of shape memory properties with self-healing polymers is a new approach that has great promise to allow in-operation healing of damage. Also, the shape memory properties of polymers can be activated under the same thermal energy that is a required stimulus for the DA healing mechanism. Therefore, thermal stimulus is the only external stimulus for both closing the cracks and healing the damages in this type of intrinsic system.

1.3.2 Adaptable, Inexpensive Maleimide Moiety Synthesis

An inexpensive synthesis method for N-(2-Hydroxyethyl)-maleimide (HEM) is studied during this research since maleimide molecules are generally expensive to purchase as commercial chemicals. Therefore, the synthesis methods focus on low cost
techniques that are commercially scalable. Optimizations are needed based on the
syntheses from Heath et al.’s method and the high purity HEM is obtained through a
three step procedure. All the characterization, analyses, and testing in this research are
conducted on the specimens with the synthesized HEM and other commercialized
monomers.

1.3.3 Directly Connected DA Healing Molecules

A self-healing polymer that grafts DA moieties directly to the main chain is
developed and successfully characterized in this research. This provides a one phase
polymer system and therefore the compatibility or unexpected reaction between healing
molecules and other monomers are not a problem in this network. A polyurethane
polymer network is utilized in order to include comparable mechanical properties to
commercial epoxy.

1.3.4 Bulk Specimens by Solvent-Free Polymerization Methods

In order to synthesize bulk specimens for testing, a solvent-free polymerization
method is employed. For the self-healing polymer with the DA reaction between furan
and maleimide, the specimens are prepared by heating up the resin above the melting
temperature to obtain molten liquid monomers. For the polymer with the DA reaction
between anthracene and maleimide, pre-polymerization is first conducted to create
isocyanate-end liquid monomer and then the rest of the polymerization steps can
proceed without the use of solvent. Acquiring solvent-free liquid resins can expand the
potential application for the polymer and even the CFRP composites can be fabricated
using the liquid resins.
1.3.5 New Methods to Accurately Measure Transition Temperatures

The DA reaction between maleimide and furan moieties and its reversibility are confirmed by using variable temperature nuclear magnetic resonance (VT NMR). In general, NMR is a great characterization technique to analyze the DA reaction since quantitative data is acquired. However, the VT NMR technique is more appropriate since characterization is performed at the actual reaction temperatures, and for this research, it more accurately determines the amount of reversible crosslinked and cleaved bonds. Moreover, the crosslinking DA efficiency between molecules is calculated and the kinetics of the crosslinking and cleaving are observed to estimate the reaction times.

1.3.6 Self-Healing Polymers with High Temperature Stability

The first high modulus, self-healing polymer with temperature stability beyond 240 °C is demonstrated. The high temperature stability is achieved through the increased cleaving temperature by the DA reaction between anthracene and maleimide moieties rather than between furan and maleimide. The relatively low cleaving temperature can place limits on the polymer’s use temperature. This research characterizes the healing efficiency using SBS testing, and it is the first time where bulk specimens of self-healing polymers using anthracene as a diene molecule are tested.

1.3.7 Self-Healing CFRP Composites with Healable Matrix

Self-healing CFRP composites with as-received carbon fiber fabrics and a thermo-responsive, self-healing polyurethane matrix are fabricated, and their healing abilities are then analyzed. A healable matrix synthesized with the DA reaction is accomplished and can be healed repeatedly in the CFRP composites. This research demonstrates the first fabrication of CFRP composites which incorporate the DA
reaction between anthracene and maleimide. Also, the composite fabrication was performed using a high melting point monomer via the isocyanate terminated pre-polymerization method where the solid monomer can become a liquid resin. The maximum loads are determined through SBS testing in order to calculate the healing efficiency of the composites.
CHAPTER 2
SELF-HEALING POLYURETHANES WITH SHAPE RECOVERY

2.1 Chapter Introduction

The development of self-healing polymers has grown over the past decade due to their ability to repair damage occurring before complete failure. Current methods have allowed for the development of self-healing polymers that are able to achieve strong healing performance, but the healing processes for these polymers are either not inherently repeatable (i.e., capsule based\textsuperscript{3,12,103-105} and vascular based\textsuperscript{11,13,62,106-109}) or require the use of an external pressure to close the crack and bring the surfaces into contact\textsuperscript{16,17,89-92}. While many promising self-healing methods are under development, to date, polymers that utilize the Diels-Alder (DA) reaction have been the most promising since it is highly efficient, simple and can be repeatedly healed through only the application of heat. Furan and maleimide groups have been the most used diene and dienophile candidates for developing self-healing polymer systems since they are highly reactive due to their lower reaction energy\textsuperscript{16,53,78,92,110-112}. This high reactivity is due to electron withdrawing ketones in maleimide and furan’s locked cis conformation that is thermodynamically less stable due to steric repulsion and therefore more reactive\textsuperscript{77}.

The DA reaction is a thermally reversible reaction between a conjugated diene and a dienophile resulting in a cyclohexene derivative\textsuperscript{71}. The crosslinked DA adducts can undergo the reverse reaction at higher temperatures, which is known as a retro DA (rDA) reaction where the two constituents are cleaved\textsuperscript{72}. Chen et al. determined the new $\sigma$ bond energy between a furan and maleimide of the DA adduct with differential

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scanning calorimetry (DSC)\textsuperscript{17}. The bond energy of the new C-C $\sigma$ bond in the DA adducts was 96.2 kJ/mol\textsuperscript{17} while other covalent bond energies are reported as 348 kJ/mol for C-C bonding, 293 kJ/mol for C-N bonding, and 389 kJ/mol for N-H bonding\textsuperscript{84}. This implies that covalent bonds are at least 3 to 4 times stronger than the intermolecular C-C $\sigma$ bond between the DA adducts. Therefore, cracks are more likely to propagate through new C-C $\sigma$ bonds than the other bonds. Consequently, healing is possible on the crack surfaces through the recovery of broken DA crosslinks and the healing efficiency directly correlates to the degree of crosslink recovery. The temperature ranges for the DA and rDA reactions are also advantageous. The DA reaction occurs at temperatures between room temperature and approximately 90 °C without any other external stimulus\textsuperscript{85}. Thus, DA polymers can still counteract the propagation of micro-damage at ambient temperature. Also, the range for the rDA reaction is approximately 130 °C, which is low enough to avoid thermal degradation of the polymer upon heating and high enough for many applications\textsuperscript{85} such as a structural composite or electronic device coating materials.

When considering self-healing polymers with the DA reaction, the major limitation of the current healing processes is the need for external forces to bring the two crack surfaces together. It is hypothesized that the shape memory effect from shape memory polymers (SMPs) can replace the use of external force. SMPs are a group of polymers that have the capability of recovering their permanent shape upon the application of an external stimulus, even after significant deformation\textsuperscript{97}. This is possible due to what is known as the shape memory effect.
An advantage of SMPs is their versatility since they can be synthesized to have a wide range of properties depending on the chemical structures and compositions\(^9^9\). According to Lendlein et al., the shape memory effect arises from the combination of the structure and the morphology of the polymers. In SMPs, two notable features exist; a soft segment (switching segment) and a hard segment (netpoint)\(^1^0^0\). The temporary shape of an SMP is fixed in a soft segment that consists of the chains, while the permanent shape is memorized in a hard segment that can consist of covalent bonds or intermolecular interactions\(^9^7,1^0^0,1^0^1\).

Recently, Rodriguez et al.\(^1^1^3\) and Luo and Mather\(^1^1^4\) reported shape memory assisted self-healing polymers (SMASH). In both papers, the shape memory properties originated from the covalent bonds (a hard segment); the network poly(\(\varepsilon\)-caprolactone) (PCL)\(^1^1^3\) and the epoxy matrix\(^1^1^4\) and the healing mechanism was due to the diffusion of PCL, which is a thermoplastic polyester with a relatively low melting point below 60 °C\(^1^1^5\). In both works, two different types of polymers (shape memory type and thermoplastic PCL) were blended and PCL was melted and flowed to heal the surfaces after the cracks were closed through the shape memory effect. One of the biggest drawbacks of these SMASHs comes from the low melting point of PCL, resulting in the limitation of application temperature ranges to below 60 °C. However, the synthesized polymers in Chapter 2 are applicable up to 130 °C before the C-C σ bonds cleave and are thermally stable up to 250 °C. Also, these polymers combine both self-healing and shape memory properties such that no external forces are required to heal a cracked surface. In order to increase stability while maintaining good mechanical properties, a thermoset polyurethane polymer system was chosen and the previously published
shape memory polyurethane by Wilson et al.\textsuperscript{101} was adapted into the developed polymers with the DA self-healing mechanism to create one complete polymer network. This has allowed for more in depth testing and characterization on the self-healing property in this work. All DA monomers were designed to connect to the polyurethane’s main chain and as a result, the DA monomers require a hydroxyl functional group such that they can react with the isocyanate functional groups to form polyurethane.

2.2 Polymer Syntheses

2.2.1 Materials

Furfuryl alcohol (FA, Acros Organics), hexamethylene diisocyanate (HDI, Acros Organics), triethanolamine (TEA, Sigma-Aldrich), and N,N,N',N'-tetrakis(hydroxypropyl)ethylenediamine (HPED, Sigma-Aldrich) were used as received. The maleimide monomer, N-(2-Hydroxyethyl)-maleimide (HEM), was prepared with DA and rDA cycloaddition through a three steps process as shown in Figure 2-1. A slightly modified version of Heath et al.’s method\textsuperscript{116} was mainly used. For the HEM synthesis, maleic anhydride (Alfa Aesar), furan (Acros Organics), ethanolamine (Acros Organics), methanol (Fisher Chemical) and toluene (Fisher Chemical) were used as received.

![Figure 2-1. Three steps synthesis of N-(2-hydroxyethyl) maleimide.][1]


2.2.2 4,10-Dioxatricyclo[5.2.1.0\textsuperscript{2,6}]dec-8-ene-3,5-dione (1)

Maleic anhydride (30 g, 305.94 mmol) and furan (21g, 308.51 mmol) were mixed and stirred in toluene (300 ml) at room temperature for 24 hours. A slightly greater
amount of furan was added than maleic anhydride to ensure all maleic anhydride, the limiting reactant, were crosslinked with furan. After 24 hours, a fine white solid powder was precipitated and the mixture was vacuum filtered and dried to obtain the product (1). Unreacted furan was filtered during the vacuum filtration process and a further purification step is not necessary (yield 85.6%). mp 123 °C; $^1$H NMR (300 Hz, DMSO-d6) δ 6.59 (s, 2H), 5.36 (s, 2H), 3.32 (s, 2H) ppm; $^{13}$C NMR (300 Hz, DMSO-d6) δ 171.98, 137.30, 82.11, 49.53 ppm

2.2.3 4-(2-Hydroxy-ethyl)-10-oxa-4-aza-tricyclo[5.2.1.02,6]dec-8-ene-3,5-dione (2) 4,10-Dioxatricyclo[5.2.1.02,6]dec-8-ene-3,5-dione (1) (30 g, 180.58 mmol) and methanol (60 ml) were added to a flask and the mixture was chilled in an ice bath for 15 minutes. A mixture of ethanolamine (11.04 g, 180.75 mmol) and methanol (5 ml) was slowly added over 30 minutes to the flask in the ice bath while stirring. The product (1) was dissolved completely into methanol while adding ethanolamine. The final mixture was then chilled in the ice bath for 30 minutes and then allowed to return to room temperature over an additional 30 minutes. Then, the solution was refluxed for 24 hours. Afterwards, the solution was cooled down and a slightly yellowish solid powder was crystallized. This powder (2) was then vacuum filtered and dried (yield 46.6%). mp 142 °C; $^1$H NMR (300 Hz, DMSO-d6) δ 6.53 (s, 2H), 5.10 (s, 2H), 4.74 (br, 1H), 3.40 (br, 4H), 2.90 (s, 2H) ppm; $^{13}$C NMR (300 Hz, DMSO-d6) δ 176.93, 136.89, 80.73, 57.73, 47.57, 41.06 ppm

2.2.4 N-(2-Hydroxyethyl)-maleimide (HEM) 4-(2-Hydroxyethyl)-10-oxa-4-aza-tricyclo[5.2.1.02,6]dec-8-ene-3,5-dione (2) (30 g) was refluxed in toluene (180 ml) for over 24 hours until it was completely cleaved. To confirm the cleaving, NMR was used and the 6.520 ppm and 5.104 ppm peaks
disappeared once furan was removed from 4-(2-Hydroxyethyl)-10-oxa-4-aza-
tricyclo[5.2.1.02,6]dec-8-ene-3,5-dione (2). The solution was cooled down, and the
white powder which crystallized was collected by vacuum filtration. (yield 83.0%); mp
75 °C; $^1$H NMR (300 Hz, DMSO-d6) δ 6.97 (s, 2H), 4.80 (br, 1H), 3.44 (br, 4H) ppm; $^{13}$C
NMR (300 Hz, DMSO-d6) δ 171.53, 134.88, 58.37, 40.38 ppm

2.2.5 Pre-crosslinking DA Adducts (DA)

To make sure that all DA adducts were completely crosslinked before testing,
HEM and FA were precrosslinked by using the DA reaction before the polymerization
step as shown in Figure 2-2. For HEM and FA, each monomer was added into toluene
with a 1:1 molar ratio and then the mixtures were heated to 75 °C while stirring for 12
hours until a light yellowish precipitation was observed. The product was then vacuum
filtered and washed twice with ether (yield 90.1%). Then, it was dried in a vacuum oven
at 80 °C for 24 hours. mp 109 °C; $^1$H NMR (300 Hz, DMSO-d6) δ 6.52 (br, 2H), 5.07 (s,
1H), 4.92 (br, 1H), 4.75 (br, 1H), 4.01 (d, 1H), 3.71 (d, 1H), 3.41 (s, 4H), 3.03 (d, 1H),
2.89 (d, 1H) ppm; $^{13}$C NMR (300 Hz, DMSO-d6) δ 176.85, 175.40, 138.53, 136.91,
92.07, 80.63, 59.40, 57.74, 50.39, 48.21, 41.00 ppm

![Figure 2-2. A schematic of the precrosslinked FA and HEM. [Reprinted with permission from Heo, Y. & Sodano, H. A. Self-Healing Polyurethanes with Shape Recovery. Adv. Funct. Mater. 24, 5261-5268, (2014)]]
2.2.6 Polymers

Commercial FA and synthesized HEM were employed for the self-healing property through the DA reaction, and TEA and HDI were adapted for the shape memory properties\textsuperscript{101}. The polyurethanes that were synthesized for testing consisted of 1 mole of DA monomer (precrosslinked FA and HEM), 1 mole of TEA, and 2.5 moles of HDI for 1DA1T polymer and 1.5 moles of DA monomer, 1 mole of TEA and 3 moles of HDI for 1.5DA1T and lastly 2 moles of DA monomer, 1 mole of HPED and 4 moles of HDI for 2DA1H. Maleimide moieties are usually solid at room temperature and have high melting points compared to the rest of the monomers (i.e., FA, TEA, HPED, and HDI). A bulk or film polymerization method utilized by other researchers\textsuperscript{16,17,86,117-119} was used to mix and dissolve the monomers into a solvent and then the solvent was allowed to evaporate slowly to acquire the polymer products. However, if the solvent is not completely removed during this process, the material properties of a polymer could end up changing. In order to avoid this potential problem, in this work, the solid DA monomers were melted at 105 °C and then they were mixed with the rest of monomers (TEA, HPED, and HDI) at the same temperature. Next, the mixture was poured into Teflon molds and placed into a preheated oven at 100 °C under nitrogen. The temperature was increased to 125 °C over one hour with a two hour dwell time. After, the specimen was decreased to 90 °C over one hour and kept at this temperature for two hours before finally cooling down to 70 °C over one hour with a two hour dwell time. The polymerization temperature profile is similar to the healing process and is designed to maximize the amount of crosslinking in the polymer after the reaction has reached completion. This polymerization processed with the HEM monomer and the polyurethane structure is shown in detail below (see Figure 2-3).
Figure 2-3. A schematic of the polymerization reaction with DA, TEA, and HDI monomers. [Reprinted with permission from Heo, Y. & Sodano, H. A. Self-Healing Polyurethanes with Shape Recovery. Adv. Funct. Mater. 24, 5261-5268, (2014)]

2.3 Characterization of the Diels-Alder Reaction

2.3.1 Thermal Analysis of the Polymers

Thermogravimetric analysis (TGA, TA Q50) was utilized to verify the polymer decomposition temperature. The TGA data also can be used to estimate the maximum temperature following DSC. Each sample with a mass of approximately 15 mg was first placed in a platinum pan. The temperature was increased from 20 °C up to 600 °C with a heating rate of 20 °C/min under a nitrogen atmosphere. The balance purge flow and sample purge flow of nitrogen were set at 40 mL/min and 60 mL/min, respectively. The results are shown in Figure 2-4 and it is clearly seen that all three specimens start decomposing above 250 °C. Therefore, these results indicate that the developed polyurethanes are thermally stable up to 250 °C, even after the cleaving reaction occurs. Moreover, these TGA data were used to design the temperature profiles of the DSC to safely increase temperatures to 160 °C so that the actual temperatures for the crosslinking and cleaving transitions can be determined.
DSC (TA Q20) was used for thermal analysis to determine the glass transition, crosslinking, and cleaving temperatures of each polymer. For testing, each polymer sample was preheated at 130 °C for 2 hours and then quenched in an ice bath. This procedure was necessary to promote cleaved bonds in the polymer structures so that the crosslinking transition which is observed at lower temperature can be shown clearly. Then, samples that weighted between 10 mg and 15 mg were placed in a standard Tzero aluminum pan. Two aluminum pans with and without samples were put on each sensor platform. The temperature ranges for DSC testing were from -10 °C to 160 °C
under the nitrogen atmosphere and the sample purge flow rate of nitrogen was set at 50 mL/min. In more detail, a sample was cooled down to an equilibration temperature of -10 °C for 2 minutes and linearly heated up to 160 °C with a ramping rate of 10 °C/min. After data acquisition, all data were analyzed using “TA Universal Analysis” software offered by TA Instruments.

The mechanism for the reversible DA reaction between FA and HEM is shown in Figure 2-5A and the temperature ranges of crosslinking and cleaving in the polymers were studied using DSC as shown in Figure 2-5B. From the DSC data, the average transition temperatures of six specimens of 1DA1T, 1.5DA1T, and 2DA1H are obtained and shown in Table 2-1. The average glass transition temperatures (42.4 °C for 1DA1T, 45.6 °C for 1.5DA1T, and 49.7 °C for 2DA1H) of the polymers are shown in the first transition in Figure 2-5B. Also, the second and third transitions in Figure 2-5B indicate the crosslinking temperature (the average of 97.3 °C for 1DA1T, 96.6 °C for 1.5DA1T, and 96.3 °C for 2DA1H) and the cleaving temperature (the average of 131.6 °C for 1DA1T, 129.3 °C for 1.5DA1T, and 129.6 °C for 2DA1H). These transition temperatures in the three different polymers are very similar for the reversible DA reaction between FA and HEM monomers in the polyurethane network. Moreover, they are slightly higher when compared to the reported DA and rDA reaction temperatures (i.e., 93 °C and 120 °C, respectively). These increased transition temperatures can be attributed to the requirement for additional thermal energy to overcome the bonding energies between all the molecules in the polymer such that the molecules become sufficiently mobile, showing that the polymer network is very stable.
Figure 2-5. Representative differential scanning calorimetry data of 1DA1T, 1.5DA1T and 2DA1H. Crosslinking and cleaving transitions are marked. [Reprinted with permission from Heo, Y. & Sodano, H. A. Self-Healing Polyurethanes with Shape Recovery. *Adv. Funct. Mater.* **24**, 5261-5268, (2014)]

Table 2-1. The average glass transition temperature, crosslinking temperature, and cleaving temperature and their standard deviations for 1DA1T, 1.5DA1T and 2DA1H.

<table>
<thead>
<tr>
<th>Temperatures</th>
<th>1DA1T</th>
<th>Standard Deviation</th>
<th>1.5DA1T</th>
<th>Standard Deviation</th>
<th>2DA1H</th>
<th>Standard Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass Transition [°C]</td>
<td>42.4</td>
<td>2.06</td>
<td>45.6</td>
<td>3.77</td>
<td>49.7</td>
<td>5.7</td>
</tr>
<tr>
<td>Crosslinking [°C]</td>
<td>97.3</td>
<td>2.45</td>
<td>96.6</td>
<td>1.53</td>
<td>96.3</td>
<td>2.3</td>
</tr>
<tr>
<td>Cleaving [°C]</td>
<td>131.6</td>
<td>2.66</td>
<td>129.3</td>
<td>2.48</td>
<td>129.6</td>
<td>3.2</td>
</tr>
</tbody>
</table>
2.3.2 Reversibility of the Self-Healing Mechanism

In order to study the reversibility of the DA reaction and retro DA reaction, variable temperature nuclear magnetic resonance (VT NMR) was utilized to observe new σ bond peaks (i.e., 6.52 ppm and 5.18 ppm for $^1$H NMR, and 91.8 ppm and 80.5 ppm for $^{13}$C NMR) in the chemical shifts. VT NMR was a better tool to analyze the actual amount of the DA reversibility since this reaction is temperature dependent and the bonding information, especially of the cleaved bonding, could be acquired at the reaction temperatures. With traditional NMR, a specimen after cleaving would need to be immediately quenched down to a lower temperature and kept at a low temperature to maintain the cleaved bonds. Otherwise, some crosslinking could occur due to the sample being at an ambient temperature making that the cleaving NMR data not representative of what actually occurs at cleaving temperatures. Thus, VT NMR is better for investigating the amount of the cleaved bonds and their reversibility. Moreover, the crosslinking and cleaving times can be estimated by repeatedly scanning the peaks until the reactions are complete. These recorded reaction times and temperatures were then used to design the healing process.

An Inova 2 500 MHz VT NMR instrument was used and deuterated dimethyl sulfoxide (DMSO-d$_6$) was used as the solvent for all the NMR specimens. A specimen was heated up by using an internal heating function of the Inova 2 instrument and cooled down with an external liquid nitrogen cooling system in air. For the VT NMR testing, the precrosslinked DA monomers were tested as a model system to evaluate the feasibility of the crosslinking/cleaving reactions between HEM and FA monomers, which contain the healing property in the polymers.
For the proton VT NMR, a sample was kept at 140 °C for 30 minutes for the cleaving process (Figure 2-6A) and was then cooled down to 80 °C for 120 minutes for the crosslinking DA reaction (Figure 2-6B). To confirm the repeatability of the reactions, the sample was re-heated to 140 °C and maintained at this temperature for 30 minutes (Figure 2-6C) and finally re-cooled down to 80 °C for 120 minutes for the crosslinking DA reaction (Figure 2-6D). As clearly shown in Figure 2-6B and 2-6D, two peaks at 6.52 ppm and 5.08 ppm appear as HEM and FA monomers are connected at 80 °C. These peaks were identified by comparing the NMR data of product (2) and of HEM in the Appendix, which was obtained during HEM monomer synthesis. The actual NMR peaks are provided as Figure A-3 and A-5 in the Appendix. As furan is removed from product (2), the 6.52 ppm and 5.08 ppm peaks disappear in the NMR data, meaning that these peaks indicate the new σ bond was created through the DA reaction. Then, as shown in Figure 2-6A and 2-6C, the two peaks disappear as the temperature increases to 140 °C since the crosslinked HEM and FA monomers become disconnected. These four NMR spectra indicate that the DA reaction occurs repeatedly between the HEM and FA monomers. However, the residue peaks of the new σ bonds still appear for the cleaved cases (shown in Figure 2-6A and 2-6C) even though the specimen and solvent in the NMR tube was kept at 140 °C until the peaks did not show any changes. During the healing process on the solid specimens, mobility of the molecules might decrease even more. Thus, this indicates that the rDA reaction is not 100% efficient, meaning that the DA and rDA reversibility was not 100% effective. This can help to possibly explain the imperfect healing efficiencies.
Figure 2-6. Proton VT NMR data for HEM and FA precrosslinked monomer to see the Diels-Alder reversibility; the precrosslinked monomer was A) kept at 140 °C for 30 minutes (cleaving, rDA reaction), B) cooled down to 80 °C for 120 minutes (crosslinking, DA reaction), C) heated up to 140 °C for 20 minutes (cleaving, rDA reaction), and D) cooled to 80 °C for 120 minutes (crosslinking, DA reaction). [Reprinted with permission from Heo, Y. & Sodano, H. A. Self-Healing Polyurethanes with Shape Recovery. *Adv. Funct. Mater.* **24**, 5261-5268, (2014)]

In this work, carbon VT NMR was also performed and example results for one sample are shown in Figure 2-7. Similar to the proton VT NMR, the sample was prepared as a solution of the crosslinked DA monomer and deuterated dimethyl sulfoxide (DMSO-d$_6$) solvent in an NMR tube. Thus, the cleaving process was first initiated by heating the tube inside the NMR chamber at 140 °C for 30 minutes. Then, for the crosslinking process, the temperature was reduced and the NMR tube was kept at 80 °C for 90 minutes. This process was performed twice to confirm the reversibility.
and repeatability of both the crosslinking and the cleaving reactions. As shown in Figures 2-7A and 2-7C, two peaks at 91.8 ppm and 80.5 ppm disappear during cleaving at 140 °C. As seen in Figures 2-7B and 2-7D, these peaks reappear when the crosslinking process occurs at 80 °C. The two peaks of 91.8 ppm and 80.5 ppm indicate the carbons that are located on the new C-C bonds from the DA reaction and the positions of two carbons are added in the DA monomer structure in Figure 2-7.

Figure 2-7. Carbon VT NMR of the DA monomer at two different temperatures to confirm the reversibility of the DA and rDA reactions. The crosslinked DA monomer was A) kept at 140 °C for 30 minutes (cleaving, rDA reaction) and B) cooled down and kept at 80 °C for 90 minutes (crosslinking, DA reaction). To test the repeatability, the temperature was C) increased to 140 °C again for 30 minutes (cleaving, rDA reaction) and finally D) lowered to 80 °C and maintained for 90 minutes (crosslinking, DA reaction). [Reprinted with permission from Heo, Y. & Sodano, H. A. Thermally responsive self-healing composites with continuous carbon fiber reinforcement. Compos. Sci. Technol. 118, 244-250, (2015)]
2.4 Characterization of Healing Performance of Polymers

2.4.1 Testing Method

In order to calculate the healing efficiency, the peak loads to induce fracture in the glassy state of the as-casted and healed specimens were measured with compact tension (CT) testing. This testing was conducted using an Instron 5969 at room temperature. The ASTM D 5045 standard was followed with slight modifications to the specimen dimensions as shown in Figure 2-8. These CT test specimens with a pin-pin configuration and slightly modified dimensions were constructed using a computer numerical control (CNC) mill. The first modification of the ASTM standard was the addition of a resting hole along the crack path to terminate the propagation in the middle of the sample. This termination was needed since the shape memory effect arises from the portion of the sample that is left intact and the polymers exhibit uncontrolled crack growth in their glassy state. In addition, the notch length was shortened to enhance the shape memory effect.

![Figure 2-8. Dimension of a compact tension test specimen (unit in inches) with a thickness of 0.35”](image)

A constant opening rate for each type of polymer specimen was used during all tests (3 mm/min for 1DA1T, 1 mm/min for 1.5DA1T, and 0.5 mm/min for 2DA1H). The opening rates were adjusted to initiate crack propagation without deforming the samples, avoid crazing, and to ensure the crack stopped at the resting hole. Under the ASTM D 5045 standard, results from at least five specimens are required to obtain reliable values. Thus, six specimens were tested for 1DA1T and eight specimens were examined for 1.5DA1T and 2DA1H. A greater number of 1.5DA1T and 2DA1H specimens were tested in order to achieve better statistical stability since the results of the initial six specimens varied. Using the initial and post healing maximum loads measured with CT testing, the healing efficiency was calculated using Equation (1)\(^ {120} \).

\[
\text{Healing Efficiency (\%)} = \frac{\text{Max. Load}_{\text{healed}}}{\text{Max. Load}_{\text{initial}}} \times 100
\]  

(1)

2.4.2 Healing Process

After a crack was formed in the specimens, and without the use of an external force to close the crack, the CT specimens were placed face-down in a vacuum oven under a nitrogen environment such that no gravitational forces contributed to the crack closure. The temperature profile for the healing process was designed to have enough time to crosslink and cleave based on the VT NMR data. The oven was slowly heated up to 135 °C over 2.5 hours and kept at this temperature for two hours. Then, the specimens were cooled down to 90 °C over one hour and kept at this temperature for two hours and finally cooled to 70 °C over one hour and kept again at this temperature for another 2 hours. The specimens were heated up to a temperature above the cleaving temperature so that the unbroken bonds could separate into two individual molecules. This process allowed for a greater chance to heal the cracks when
undergoing the DA reaction since it may be difficult for the crack faces in the polymer to align and recover their exact prior positions to allow the formation of identical bonds. Also, 2 hour rest steps were taken at 90 °C and 70 °C since the gradual temperature changes ensured that the specimens were cooled uniformly. Figure 2-9 shows a cracked specimen before (left) and the same specimen after the thermal healing process (right).

Figure 2-9. Images of a specimen after cracking (left) and after the thermal healing process without the use of external forces (right). [Photo courtesy of Heo Y. and Sodano H.] [Reprinted with permission from Heo, Y. & Sodano, H. A. Self-Healing Polyurethanes with Shape Recovery. Adv. Funct. Mater. 24, 5261-5268, (2014)]

2.4.3 Healing Performance

Figure 2-10 presents example CT test results for a specimen of 1DA1T, 1.5DA1T, and 2DA1H (A, B, and C, respectively). For the first, second, and third healing processes, efficiencies of 79.8%, 69.3%, and 59.3% for 1DA1T, 84.1%, 84.3%, and 75.9% for 1.5DA1T, and 96.1%, 82.1% and 79.7% for 2DA1H, respectively, were calculated and shown in Table 2-2 and the error bars as shown in Figure 2-10D indicate the standard deviation of the multiple specimens. Based on these results, the polymer that exhibited the higher and more stable healing performance is 2DA1H. This result is attributed to the greater amount of available furan and maleimide molecules to heal the crack surfaces, when compared to 1DA1T and 1.5DA1T.
Figure 2-10. Maximum loads from the compact tension testing as a function of extensions after the first, second, and third healing cycles for a specimen of A) 1DA1T, B) 1.5DA1T, and C) 2DA1H. D) The average healing efficiencies of 1DA1T, 1.5DA1T, and 2DA1H for the first, second, and third healing. The error bars indicate the standard deviation. [Reprinted with permission from Heo, Y. & Sodano, H. A. Self-Healing Polyurethanes with Shape Recovery. *Adv. Funct. Mater.* **24**, 5261-5268, (2014)]

Table 2-2. The average healing efficiencies and standard deviations (SD) of the 1DA1T, 1.5DA1T, and 2DA1H polyurethane specimens.

<table>
<thead>
<tr>
<th>Polyurethane</th>
<th>Healing Efficiency (SD)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1&lt;sup&gt;st&lt;/sup&gt; cycle</td>
</tr>
<tr>
<td>1DA1T</td>
<td>79.8% (9.7)</td>
</tr>
<tr>
<td>1.5DA1T</td>
<td>84.1% (14.5)</td>
</tr>
<tr>
<td>2DA1H</td>
<td>96.1% (22.5)</td>
</tr>
</tbody>
</table>
Some of these reported standard deviations indicate that there might not be a statistically significant difference in healing efficiency between subsequent healing cycles. Therefore, the hypothesis that the average healing efficiencies of the three healing cycles are equal to one another for each polymer was tested using a one way analysis of variance (ANOVA). As a result, with 95% confidence, this hypothesis was accepted for both 1.5DA1T and 2DA1H, while it was rejected for 1DA1T. These results indicate that 1.5DA1T and 2DA1H have excellent repeatable healing abilities, since essentially no drop in healing performance was observed between subsequent cycles.

The measured healing efficiency is approximately 80-96% of the virgin fracture load. There are two primary reasons that the efficiency is below 100%. The first is due to the efficiency of the re-crosslinking reaction of the DA molecules and the second relates to the sharpening of the crack tip due to fracture in the virgin sample. For the crack to completely heal the polymer network needs to be completely reformed; however, it is probable that following healing, disconnected molecule pairs exist in the specimen. As shown in the VT NMR data (Figure 2-6 and Figure 2-7), the cleaving process (rDA reaction) is not 100% effective in solution and is expected to be lower in the solid state due to steric effects, which may result in diminished healing efficiency. A second explanation is that the healing mechanism is difficult to accurately measure since the crack in a healed specimen will always be sharper than the pre-crack produced in the virgin sample, and thus a higher stress intensity should exist following healing. This higher stress intensity would produce an apparent rather than true reduction in healing efficiency. The influence of this factor could be reduced through the formation of a starter crack by creating a stable crack growth process, however this was
challenging with the glassy polymer and efforts to accomplish this were unsuccessful. However, all 1DA1T, 1.5DA1T and 2DA1H polymers possess superior healing efficiencies when compared (using fracture strength) to similar polymers seen in the literature, including 2MEP4F$^{16}$ and polymer 400$^{121}$ with reported average first healing efficiencies of 80 % and 46 %, respectively.

2.4.4 Influence of Glass Transition Temperature and Molecular Mobility

The glass transition temperature of any of the polymers can be controlled by adding more aromatic rings into the polymer network while maintaining the same amount of DA molecules. Therefore, to draw general conclusions on the effect that $T_g$ has on healing performance, two different polyurethanes with varying $T_g$ were specifically synthesized. This aspect was investigated since it was believed that $T_g$ might affect the mobility of the DA molecules, and better molecular mobility leads to an increase in healing performance.

As shown in Table 2-3, the two different synthesized polyurethanes were 1DA1T-0TDI and 1DA1T-0.5TDI. The polymer with the lower $T_g$ (1DA1T-0TDI) was created by synthesizing 1 mole of DA, 1 mole of TEA, and 2.5 moles of HDI. The polymer with the higher $T_g$ (1DA1T-0.5TDI) was prepared by adding an additional molar fraction of toluene diisocyanate (TDI), which contains one aromatic ring. Between these two polymers, the moles of DA and TEA were kept the same, but 2 moles of HDI and 0.5 moles of TDI were used to synthesize 1DA1T-0.5TDI. As with all the other previously developed polymers, CT testing was conducted to evaluate the healing efficiency (Equation 1). Results from this testing are presented in Table 2-3, and for 1DA1T-0TDI (lower $T_g$), healing efficiencies of 80%, 69%, and 59% were obtained for the first, second, and third healing cycles, respectively. For 1DA1T-0.5TDI (higher $T_g$), healing
efficiencies of 66%, 59%, and 53% were obtained for the first, second, and third healing cycles, respectively. Since larger standard deviation values were observed for 1DA1T-0.5TDI, a one way ANOVA was performed. The results indicate 1DA1T-0.5TDI has an excellent repeatable healing ability, since there is not a statistically significant difference in healing performance between subsequent cycles. Hence, these healing performance results show that by adding more aromatic rings into the polymer network while maintaining the same amount of DA molecules, the glass transition temperature increases, but the healing performance decreases.

Table 2-3. The glass transition temperatures ($T_g$) of 1DA1T-0TDI and 1DA1T-0.5TDI

<table>
<thead>
<tr>
<th>Polyurethane Molar Ratio</th>
<th>Molar Ratio</th>
<th>$T_g$ (°C)</th>
<th>Healing Efficiency (SD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DA TEA HDI TDI</td>
<td></td>
<td></td>
<td>1st Healing</td>
</tr>
<tr>
<td>1DA1T-0TDI</td>
<td>1 1 2.5 0</td>
<td>42.4</td>
<td>79.8% (9.7)</td>
</tr>
<tr>
<td>1DA1T-0.5TDI</td>
<td>1 1 2 0.5</td>
<td>56.9</td>
<td>66.3% (10.0)</td>
</tr>
</tbody>
</table>

Inherent differences in the synthesis requirements between these two polymers introduces factors that cause a comparison strictly based on just the $T_g$ to be unachievable. Nonetheless, the following discussion presents general observations regarding relationships between molecular mobility, glass transition temperature, polymer structure, and overall healing performance. When the temperature of a polymer reaches its $T_g$, the material starts becoming soft and flexible like rubber elastomers. Therefore, molecules become movable at this temperature point, and the mobility of these molecules continues to increase as the temperature increases. If the same healing temperature profile was applied simultaneously to a specimen of 1DA1T-0TDI
and a specimen of 1DA1T-0.5TDI, molecules in the lower T_g specimen (1DA1T-0TDI) start to become more mobile at a lower temperature, and as a result, at high healing temperatures, the chain mobility is higher. Thus, a higher healing efficiency can be expected since the DA molecules (furan and maleimide) have a greater chance to crosslink with one another when compared to 1DA1T-0.5TDI (higher T_g).

Due to the nature of the synthesis process when creating similar polymers with varying glass transition temperatures, inherent differences in the polymer structures occur. The polymer structure can affect both the molecular mobility and thus, the healing performance. In order to increase the T_g of a polymer, the movement of a molecular chain needs to be constrained by either creating more crosslinking bonds or by adding larger, stiffer molecules. In this study, the addition of the stiff aromatic isocyanate monomer when synthesizing 1DA1T-0.5TDI decreased the chain mobility (thus creating a polymer with a higher T_g), but more thermal energy was required to make the chain movable. Consequently, the chain mobility of the higher T_g specimen (1DA1T-0.5TDI) is lower, regardless of the healing temperatures, resulting in a lower healing efficiency.

2.4.5 Shape Memory Characterization

In addition to the self-healing property of the polyurethanes, the shape memory property was also confirmed. Shape memory polyurethanes were adapted from the previously published work by Wilson et al. whose shape memory properties were confirmed by cyclic tensile testing. However, in order to evaluate the shape memory properties of 1DA1T, 1.5DA1T, and 2DA1H, a free strain recovery capability test in two different directions under free-strain conditions was conducted and the representative results for 1.5DA1T are shown in Figure 2-11. To conduct this testing, a newly
synthesized polymer film with dimensions of 48.6 mm x 8.73 mm x 1.08 mm was heated at 100 °C for 5 minutes, stretched in the longitudinal direction, and cooled down to room temperature in order to fix the temporary shape. Then, the film was re-heated to 100 °C for 5 minutes to let the permanent shape recover. Another film with dimensions of 76.5 mm x 8.6 mm x 1.06 mm was used to show the spiral shape memory property. Similarly, this sample was heated to 100 °C for 5 minutes, coiled, and cooled down to room temperature to fix the temporary shape. Then, to recover the permanent shape, the film was re-heated to 100 °C for 5 minutes.

Figure 2-11. Images of a 1.5DA1T film show the A) permanent shape (48.6 mm x 8.73 mm x 1.08 mm), B) temporary shape after deforming and fixing, C) permanent shape after recovering, D) permanent shape (76.5 mm x 8.6 mm x 1.06 mm), E) spiral temporary shape, and F) recovered permanent shape. [Photo courtesy of Heo Y. and Sodano H.] [Reprinted with permission from Heo, Y. & Sodano, H. A. Self-Healing Polyurethanes with Shape Recovery. Adv. Funct. Mater. 24, 5261-5268, (2014)]

Figure 2-11A shows the permanent shape (dimensions of 48.6 mm x 8.73 mm x 1.08 mm) and Figure 2-11B presents the temporary shape after heating the film at
100 °C for 5 minutes, stretching the film, and then cooling it down to room temperature in order to fix the shape. Finally, Figure 2-11C displays the recovered permanent shape after heating the sample to 100 °C, which is above the glass transition temperature. An additional test was performed to show the spiral shape memory property of the polymer. Figure 2-11D shows the permanent shape (dimensions of 76.5 mm x 8.6 mm x 1.06 mm) and Figure 2-11E exhibits the coiled temporary shape at room temperature after heating the film at 100 °C for 5 minutes and fixing it. Lastly, Figure 2-11F illustrates the permanent shape of the polymer after recovery. Through these tests, it can be concluded that the developed self-healing polyurethanes contain shape recovery and this shape recovery force can be used to close the crack with the application of heat during the healing process.

2.4.6 Influence of Shape Memory Recovery Force

As previously mentioned during discussion regarding modifications to the ASTM D 5045 standard CT specimen dimensions, the pre-crack length was shortened to enhance the shape memory recovery force since the shape memory effect arises from the unbroken region. Therefore, additional testing was designed and conducted in order to determine the impact that the size of the unbroken area has on the shape memory recovery force, and ultimately the healing efficiency. Three different CT specimen Types (A, B, and C) as shown in Figure 2-12 with varying pre-crack length were developed and tested. The length of the crack path between the tip of the pre-crack and the resting hole (0.24 inches) for these different specimen types was the same, while the unbroken areas were various.
Figure 2-12. Three different Types (A, B, and C) of CT test specimens with varying pre-crack lengths.

Three different types of 1.5DA1T specimen were tested to obtain the initial and post-healed maximum loads at fracture with a 1 mm/mim opening rate during the CT testing, and these measured loads were used to calculate the healing efficiencies for three healing cycles. As shown in Table 2-4, the average healing efficiencies for the Type C specimen with the smallest shape memory recovery force were the lowest. Moreover, it was observed that the healed area on the specimen only came close to the resting hole after the healing process. This result indicates that the shape memory recovery force was not sufficient for the Type C specimens to completely close the crack surfaces, resulting in the broken DA bonds not reforming. When comparing the efficiencies between the Type A and Type B samples, the first healing cycle efficiencies are similar to each other but for the second healing cycle, the Type B specimen had a much larger decrease. This indicates that the Type B specimen was unable to provide a satisfactory amount of shape memory recovery force needed for repeatable healing performance.
Table 2-4. The average healing efficiencies and standard deviations (SD) for three different 1.5DA1T specimen Types (A, B, and C).

<table>
<thead>
<tr>
<th>Healing Cycle</th>
<th>1.5DA1T-A Healing Efficiency</th>
<th>SD</th>
<th>1.5DA1T-B Healing Efficiency</th>
<th>SD</th>
<th>1.5DA1T-C Healing Efficiency</th>
<th>SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>1(^{st}) healing</td>
<td>84.1%</td>
<td>14.5</td>
<td>83.7%</td>
<td>5.7</td>
<td>67.8%</td>
<td>11.1</td>
</tr>
<tr>
<td>2(^{nd}) healing</td>
<td>84.3%</td>
<td>7.8</td>
<td>61.7%</td>
<td>14.5</td>
<td>48.4%</td>
<td>19.6</td>
</tr>
<tr>
<td>3(^{rd}) healing</td>
<td>75.9%</td>
<td>12.6</td>
<td>43.6%</td>
<td>5.4</td>
<td>29.9%</td>
<td>21.9</td>
</tr>
</tbody>
</table>

2.4.7 Mechanical Properties

The mechanical properties were investigated for the self-healing polyurethanes. Samples using the ASTM 638 Type V standard were tested and a total of 12 flat specimens of each polymer (1DA1T, 1.5DA1T, and 2DA1H) were prepared to measure the ultimate tensile strength, strain, and Young's modulus. All tensile tests were done at room temperature and the opening rate of 5 mm/min was used. In addition, the maximum loads at fracture from a compact tension test were obtained to calculate the fracture toughness. The test conditions, procedures and dimensions of the specimen for the CT test were satisfied by the ASTM D 5045 standards. Each of 6 specimens was tested at room temperature on an Instron 5969 at an opening rate of 5 mm/min.

The average ultimate tensile stresses and the Young's modulus from 12 specimens were 76.8 MPa and 2.86 GPa for 1DA1T, 87.3 MPa and 2.48 GPa for 1.5DA1T, and 53.7 MPa and 2.56 GPa for 2DA1H, respectively. They are comparable to composites grade epoxy but the ultimate tensile strain of 1DA1T is much larger than epoxy. This indicates that 1DA1T, 1.5DA1T, and 2DA1H still exhibit elastomeric behavior as a result of the TEA or HPED and HDI polyurethanes even after adding DA
crosslinking to the polymer. For fracture toughness, a total of six specimens of each polymer were tested and 1.43 MPa for 1DA1T and 1.06 MPa for both 1.5DA1T and 2DA1H were obtained. All average fracture toughness are more than that of an epoxy.

In Table 2-4, all data are listed and the standard deviations of each property are also shown. These data were compared to composite grade epoxy since the developed polyurethane was studied as a possible substitute to epoxy fractions in structural composites, also generally known as polymer matrix composites.

Table 2-5. Comparison of mechanical properties between 1DA1T, 1.5DA1T, 2DA1H, and epoxy.

<table>
<thead>
<tr>
<th>Property</th>
<th>1DA1T</th>
<th>Standard Deviation</th>
<th>1.5DA1T</th>
<th>Standard Deviation</th>
<th>2DA1H</th>
<th>Standard Deviation</th>
<th>Epoxy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ultimate tensile strength [MPa]</td>
<td>76.8</td>
<td>8.2</td>
<td>87.8</td>
<td>7.6</td>
<td>53.7</td>
<td>18.8</td>
<td>35-130\textsuperscript{122}</td>
</tr>
<tr>
<td>Ultimate tensile strain [%]</td>
<td>30.5</td>
<td>23.5</td>
<td>5.4</td>
<td>2.8</td>
<td>2.3</td>
<td>0.9</td>
<td>2-5\textsuperscript{123}</td>
</tr>
<tr>
<td>Young's modulus [GPa]</td>
<td>2.4</td>
<td>0.3</td>
<td>2.6</td>
<td>0.2</td>
<td>2.6</td>
<td>0.3</td>
<td>2-6\textsuperscript{122}</td>
</tr>
<tr>
<td>Glass transition temperature [°C]</td>
<td>42.4</td>
<td>2.1</td>
<td>45.6</td>
<td>3.8</td>
<td>49.7</td>
<td>5.7</td>
<td>50-250\textsuperscript{122}</td>
</tr>
<tr>
<td>Fracture toughness [MPa·√m]</td>
<td>1.4</td>
<td>0.1</td>
<td>1.1</td>
<td>0.04</td>
<td>1.1</td>
<td>0.2</td>
<td>0.6\textsuperscript{124,a)}</td>
</tr>
</tbody>
</table>

\textsuperscript{a)} Epoxy resin (L135i) with an amine hardener (H137i)

2.5 Chapter Summary

In this chapter, the development of thermo-responsive self-healing polyurethanes that can be repeatedly healed without using the application of external force was demonstrated. This was possible by synthesizing polymers which combine two functionalities – self-healing and shape memory properties and therefore, the same
thermal energy required for healing could be used for the shape memory properties to close the crack. The integration of shape memory properties with self-healing polymers is a new approach that has great promise for applications where in-place healing of damage would be beneficial.

Additionally, the synthesis methods focused on low cost techniques that are commercially scalable. The polyurethane backbone created excellent mechanical properties comparable to epoxy, while allowing the DA monomers to link to the main polymer chains. The DA reaction between maleimide and furan moieties and its reversibility were confirmed at the actual transition temperatures by using VT NMR. The healing efficiencies calculated using maximum loads from CT testing confirmed that repeated healing without external pressure was possible with only slight loss in efficiency.
CHAPTER 3
SELF-HEALING POLYMERS WITH HIGH TEMPERATURE STABILITY

3.1 Chapter Introduction

Reversible Diels-Alder (DA) cycloaddition is one of the most promising and commonly selected mechanisms used in intrinsic self-healing systems due to the reaction’s simplicity, reversibility, and repeatability. The DA reaction is a reversible reaction between a conjugated diene and a dienophile. These two molecules can be crosslinked under thermal stimulus and a cyclohexene derivative is obtained. Also, the reverse reaction occurs at higher temperatures and the cyclohexene molecule separates back into the diene and the dienophile, called the retro DA (rDA) reaction. However, the thermally reversible nature of the DA reaction places limitations on the use temperature of the polymer making it poorly suited as an engineering material for high performance applications. As an example, furan and maleimide groups have been the most used diene and dienophile candidates for developing self-healing polymer systems, but the major limitation of using these moieties is the relatively low application temperature range that synthesized polymers possess due to the cleaving rDA reaction (approximately 120 °C). This is a critical limitation for higher temperature applications (greater than roughly 130 °C) since the polymer may become unstable, degrade or experience significant drop in Young’s modulus above the cleaving temperature due to the loss of crosslinking bonds. In an effort to expand the useful temperature range of self-healing polymers, DA/rDA reactions using anthracene as a diene have been investigated since the rDA reaction theoretically proceeds between 250 °C and 300 °C. Therefore, self-healing polymers with anthracene and maleimide should be very stable when exposed to high temperatures. However, this
temperature range is above the decomposition temperature of the anthracene and maleimide monomers and therefore, researchers have never proved cleaving occurs. Also, due to the decomposition of the individual molecules, these moieties have never been shown to exhibit self-healing using the reversible DA reaction$^{45,80}$.

Here, it is shown that the rDA reaction is not required for healing and that a high healing efficiency and thermal stability beyond 240 °C can be repeatable attained using an DA reaction between anthracene and maleimide molecules. This is possible since crack propagation can be controlled due to the lower bond energy of the C-C σ bonds from the DA reaction than the energy of the other covalent bonds. From the literature, the C-C crosslinking bond energy between anthracene and maleimide varies from 77 kJ/mol to 117 kJ/mol depending on the attached substituents$^{83}$ while the rest of the covalent bond energies are 348 kJ/mol for C-C bonding, 389 kJ/mol for N-H bonding, and 293 kJ/mol for C-N bonding$^{84}$. Thus, the crack propagates through these newly formed C-C σ bonds, and the broken bonds can be reformed after mechanical scission, providing a mechanism for self-healing and recovery of the polymer’s original properties.

Consequently, this work shows for the first time that the reversible aspect of the DA/rDA reactions is not required to achieve large and repeatable healing ability in a polymer network. Furthermore, this is the first demonstration of a self-healing DA polymer that exhibits a high use temperature. In this work, the healing behavior is demonstrated on bulk specimens and healing efficiency calculations were performed with mechanical toughness testing according to the accepted ASTM standard. Past research has found difficulty working with anthracene and maleimide molecules since
their high melting point has required the use of solvent polymerization which limits the specimen to a film morphology while only allows tensile testing. Here, it is shown that solvent-free pre-polymerization between the precrosslinked adduct of 9-anthracenemethanol and N-(2-hydroxyethyl)-maleimide (HEM) and hexamethylene diisocyanate (HDI) can yield a viscous liquid monomer that can be reacted as a crosslinker. To the best of the authors’ knowledge, this is the first report of the synthesis and characterization of bulk polymers with anthracene and maleimide.

3.2 Polymer Preparation

3.2.1 Materials

ACS certified chemicals for N-(2-Hydroxyethyl)-maleimide (HEM) synthesis including maleic anhydride, furan, ethanolamine, methanol, and toluene were purchased and used as received. Commercial 9-anthracenemethanol from TCI Chemical, triethanolamine (TEA) from Alfa, and hexamethylene diisocyanate (HDI) from Sigma-Aldrich were purchased and also used as received.

3.2.2 HEM Synthesis

HEM was synthesized through a three step process, starting with maleic anhydride and furan as shown in Figure 3-1. Maleic anhydride (60 g, 612 mmol) and furan (42 g, 617 mmol) were initially reacted (DA reaction) in toluene (600 ml) at room temperature to protect the C=C bonds in maleic anhydride prior to the reaction with ethanolamine due to the highly reactive C=C bonds. After reacting them for 24 hours in toluene, the resulting compound (1) in Figure 3-1 was precipitated out and vacuum filtered and washed with diethyl ether. Then, compound (1) (60 g, 361 mmol) was reacted with ethanolamine (22 g, 362 mmol) in methanol (120 ml) by refluxing the mixture for 24 hours. When the methanol solution was cooled down to room
temperature, product (2) was precipitated out and vacuum filtered. The fully dried resulting product (2) (60 g) was refluxed in toluene (400 ml) to cleave the furan until the furan peaks at 6.53 ppm and 5.10 ppm were not detected in proton nuclear magnetic resonance (\(^1\)H NMR). The solution was cooled down to room temperature and the cleaved product (HEM) was crystallized and filtered. All products were fully dried in a vacuum oven for 24 hours before the next reaction was initiated.

Product 1: yield 85.6%, mp 123 °C; \(^1\)H NMR (300 Hz, DMSO-\(d_6\)) \(\delta\) 6.59 (s, 2H), 5.36 (s, 2H), 3.32 (s, 2H) ppm; \(^{13}\)C NMR (300 Hz, DMSO-\(d_6\)) \(\delta\) 172.0, 137.3, 82.1, 49.5 ppm. Product 2: yield 46.6%, mp 142 °C; \(^1\)H NMR (300 Hz, DMSO-\(d_6\)) \(\delta\) 6.53 (s, 2H), 5.10 (s, 2H), 4.74 (br, 1H), 3.40 (br, 4H), 2.90 (s, 2H) ppm; \(^{13}\)C NMR (300 Hz, DMSO-\(d_6\)) \(\delta\) 176.9, 136.9, 80.7, 57.7, 47.6, 41.1 ppm. HEM: yield 83.0%, mp 75 °C; \(^1\)H NMR (300 Hz, DMSO-\(d_6\)) \(\delta\) 6.97 (s, 2H), 4.80 (br, 1H), 3.44 (br, 4H) ppm; \(^{13}\)C NMR (300 Hz, DMSO-\(d_6\)) \(\delta\) 171.5, 134.9, 58.4, 40.4 ppm

3.2.3 Pre-Crosslinked Compounds (HTDA) Synthesis

HTDA was employed in the polymer synthesis process to ensure that all HEM and 9-Anthracenemethanol molecules were fully crosslinked before testing. The synthesis procedures were adapted from Syrett et al.’s work and slightly modified\(^{125}\). The synthesized HEM and 9-Anthracenemethanol were refluxed in toluene for 24 hours. Then, the solution was hot-filtered and cooled down to room temperature in order to produce HTDA as shown in Figure 3-1. Yield 86.4%, mp 185 °C, \(^1\)H NMR (300 Hz, DMSO-\(d_6\)) \(\delta\) 7.74 (d, 1H), 7.44 (d, 1H), 7.19 (m, 6H), 5.40 (t, 1H), 4.91 (q, 2H), 4.74 (d, 1H), 4.68 (t, 1H), 3.29 (m, 2H), 3.08 (t, 2H), 2.66 (m, 2H) ppm, \(^{13}\)C NMR (300 Hz, DMSO-\(d_6\)) \(\delta\) 177.0, 176.2, 143.0, 140.4, 139.9, 126.8, 126.6, 126.3, 125.2, 124.9, 124.1, 122.9, 58.7, 57.0, 49.8, 48.0, 45.9, 45.5 ppm
3.2.4 Polymer Synthesis

By using HTDA, TEA, and HDI, two polymers (named 0.5HTDA1T and 0.8HTDA1T) with different compositions were synthesized. To produce 0.5HTDA1T, 0.5 moles of HTDA, 1 mole of TEA and 2 moles of HDI were reacted. Similarly, for 0.8HTDA1T, 0.8 moles of HTDA, 1 mole of TEA and 2.3 moles of HDI were reacted. The steps for this polymerization process can be seen in Figure 3-2. To synthesize both polymers, the proper molar ratio of HTDA and HDI were reacted at 105 °C for approximately 3 hours until the mixture became completely transparent. The molten resin was mixed with TEA until it became one phase and then was quickly poured into a Teflon mold. The mold with resin was degassed for 30 minutes in a vacuum oven at room temperature. Then, the specimen was heated up to 125 °C over one hour and kept at this temperature for two hours. After that, the specimen was decreased to 90 °C over one hour with a two hour dwell time and finally cooled down to 70 °C over one hour and stayed for another two hours.
Self-healing polyurethanes are synthesized by initially pre-croslinking 9-anthracenemethanol and N-(2-hydroxyethyl)-maleimide (HEM) through the DA reaction to form a diol. The precrosslinked monomer (HTDA) was employed to ensure that the self-healing agents are fully crosslinked before the crack is introduced. A schematic of the HTDA syntheses process is shown in Figure 3-1.

3.3 Characterization of DA reaction

The efficiency and kinetics of the DA reaction were characterized through variable temperature proton nuclear resonance (VT $^1$H NMR) with a 500 MHz magnetic field at the reaction temperature. These are important to evaluate since the efficiency of these two molecules can be directly related to the efficiency for healing, especially when the crosslinking reaction is only employed to have specimens recover the original properties. For the NMR characterization process, 1 mole of the synthesized HEM and 1 mole of 9-anthracenemethanol were mixed in DMSO-d$_6$ solvent in a NMR tube and the reaction was prepared by dissolving the constituents in deuterated dimethyl sulfoxide (DMSO-d$_6$) solvent. Then, the mixture was heated at 140 °C by using an
internal heating function of the NMR instrument to measure the changes in the peaks as soon as the specimen reaches the target temperature of 140 °C (0 minute), and after 5 minutes, 15 minutes, 30 minutes, and 100 minutes. The NMR spectra corresponding to each heating time is shown in Figure 3-3. Proton peaks at 8.5 ppm, 8.1 ppm, and 7.5 ppm for anthracene and at 7 ppm for maleimide were used as crosslinking indicators since as more of the two molecules become crosslinked, the intensity of these peaks may reduce and eventually disappear. Therefore, the crosslinking efficiency can be easily evaluated using the $^1$H NMR spectrum. From Figure 3.3, it can clearly be seen that the peaks at 8.5 ppm, 8.1 ppm, and 7.5 ppm for the anthracene protons and the peak at 7 ppm for maleimide protons disappear as the duration of heating increases. It can be observed that the DA reaction between anthracene and maleimide progresses relatively quickly at 140 °C since most crosslinking is shown to be complete after only 5 minutes of heating. The peak at 7 ppm shifts to 6.9 ppm following cycloaddition due to changes in the neighboring protons. Therefore, the efficiency for the crosslinking DA reaction between these molecules can be concluded as close to 100% since the anthracene and maleimide peaks essentially disappear from the VT $^1$H NMR spectrum. However, as seen in Figure 3-3, some peaks still slightly appear in the spectra, indicating that the crosslinking efficiency of the solid state specimens are lower than 100% because the NMR spectrum were obtained from a liquid state specimen with better molecule mobility. These results are similar to the other VT NMR spectrums which were used when characterizing the reversibility of the DA reaction (Figures 2-6 and 2-7 in Chapter 2), meaning that the crosslinking efficiency of the DA reaction is not completely 100%. This might help to explain why healing efficiency slightly drops with each
repeatable cycle were observed. However, the peak residues are very small and nearly negligible.

![Figure 3-3. VT $^1$H NMR spectra for the kinetics of the crosslinking DA reaction; the specimen heating duration at 140 °C for A) 0 minute, B) 5 minutes, C) 15 minutes, D) 30 minutes, and E) 100 minutes.](image)

3.4 Characterization of Healing Performance

3.4.1 Healing Efficiency

The healing efficiency of the polyurethane was measured to validate if only the reformation of the broken $\sigma$ C-C bonds can lead to healing. The healing efficiency was calculated through compact tension (CT) fracture testing in order to obtain the virgin and post-healed maximum loads when the crack is induced. Four specimens of each
polyurethane were prepared with a slightly modified ASTM D 5045 configuration as shown in Figure 3-4. Two modifications were applied; a resting hole on the crack path was added to avoid catastrophic failure of the specimen and allow the crack surfaces to maintain their position and the length of pre-crack was reduced.

![Figure 3-4. Dimensions of a modified compact tension test specimen (unit in inch)](image)

Thickness = 0.35 "

Two polyurethanes were synthesized with different molar ratios of the healing DA molecules such that healing can be correlated to the fraction of reformable crosslinks. The first polymer is designated 0.5HTDA1T and consists of 0.5 moles of HTDA, 1 mole of TEA and 2 moles of HDI and the second designated 0.8HTDA1T has a greater molar fraction of the pre-crosslinked HTDA molecule and consists of 0.8 moles of HTDA, 1 mole of TEA and 2.3 moles of HDI. A schematic of the polymer network is presented in Figure 3-2.

From the CT testing, the maximum loads at fracture were obtained and used to calculate the efficiency as the maximum loads of the post-healing specimens divided by the maximum loads of the initial specimens (Equation 1). Following fracture of the
specimen, the healing was performed on a hot press with approximately 100 psi of pressure applied. The specimens were then heated for two hours each at 160 °C, 120 °C and lastly 70 °C. The specimens were then removed from the press and heated at 120 °C in an oven under ambient pressure to recover the shape and to eliminate any internal stresses that might have been created from the pressure. Representative fracture behaviors of the 0.5HTDA1T and 0.8HTDA1T samples are shown in Figure 3-4A and 3-4B, respectively. The average healing efficiencies of 0.5HTDA1T and 0.8HTDA1T are provided in Table 3-1. This table shows that, as calculated from the results of eight samples, 0.5HTDA1T exhibits a healing efficiency of 66.3%, 68.2% and 62.1% for the first, second, and third healing cycles, respectively. The case of a high molar fraction of DA crosslinks lead to significantly improved healing efficiency, with the 0.8HTDA1T samples producing a healing efficiency, from six averaged specimens, of 94%, 78% and 77% for the first, second, and third cycles, respectively. However, some of the reported standard deviations indicate that there might not be a statistically significant difference in healing efficiency between subsequent healing cycles. Therefore, the hypothesis that the average healing efficiencies of the three healing cycles are equal to one another for each polymer was tested using a one way analysis of variance (ANOVA). As a result, with 95% confidence, this hypothesis was accepted for both 0.5HTDA1T and 0.8HTDA1T, indicating that these polymers have excellent repeatable healing abilities since essentially no drop in healing performance was observed between subsequent cycles.

These average healing efficiency data show that a larger molar fraction of HTDA is required to increase the healing efficiency. A high fraction of HTDA is important since
it is believed that crack propagation occurs mostly through DA bonds due to its lower bond energy. The C-C crosslinking bond energy between anthracene and maleimide has been reported to vary from 77 kJ/mol to 117 kJ/mol depending on the attached substituents while the rest of the covalent bond energies are 348 kJ/mol for C-C bonding, 389 kJ/mol for N-H bonding, and 293 kJ/mol for C-N bonding. However, it is probable that the crack can propagate through a number of covalent bonds that cannot be recovered and thus the efficiencies for both polymers are not expected to reach 100%. In each subsequent fracture and healing cycle, more covalent bonds are damaged resulting in a decreasing healing efficiency, especially in 0.8HTDA1T. Interestingly, in contrast to 0.8HTDA1T, 0.5HTDA1T shows a nearly constant healing efficiency, which is attributed to the lower fraction of HTDA moieties. This results in more significant covalent bond damage and thus the creation of a pathway for crack propagation. With the high crosslinking efficiency of the HTDA, it is expected that the nearly constant fracture strength is solely a result of the reformed HTDA crosslinks. Figure 3-4C are images of a fractured 0.8HTDA1T specimen (left), clearly showing cracking, and of the same specimen following healing (right), clearly demonstrating the reformation of the polymer with the fracture no longer visible.

Table 3-1. The average healing efficiencies and standard deviations (SD) of the 0.5HTDA1T and 0.8HTDA1T polyurethane specimens.

<table>
<thead>
<tr>
<th>Polyurethane</th>
<th>Healing Efficiency a) (SD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5HTDA1T</td>
<td>66.3% (14.2) 68.2% (14.1) 62.1% (15.1)</td>
</tr>
<tr>
<td>0.8HTDA1T</td>
<td>94.4% (14.4) 77.8% (16.7) 76.7% (9.7)</td>
</tr>
</tbody>
</table>

a) Percentage of healing ability was calculated by dividing the post-healed maximum load by the initial maximum load
3.4.2 Thermal Analysis

The thermal stability of the polymers was investigated through thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) on two samples of each polymer. All the acquired data from TGA and DSC testing were analyzed with “TA Universal Analysis” software offered by TA instruments.

In order to investigate the decomposition temperature, TGA (TA Q50) was conducted at a heating rate of 20 °C/min up to 600 °C under a nitrogen condition.

Figure 3-4. Representative load curves as a function of extension for one, A) 0.5HTDA1T and B) 0.8HTDA1T, and C) one 0.8HTDA1T specimen showing pre- (left) and post-healing (right).
Approximately 10 mg of sample was placed on the platinum pan and the balance was purged at 40 mL/min and the sample was purged at 60 mL/min. The TGA curve shown in Figure 3-5A demonstrates that the polymer does not decompose until the temperatures reaches 251 °C for 0.5HTDA1T and 240 °C for 0.8HTDA1T. Although beyond the T_g, both polymers are stable for applications up to 240 °C.

For the polymer phase changes, DSC (TA Q20) was employed and a 10 mg specimen was placed in a Tzero aluminum pan. The specimen was cooled to -10 °C and then heated to 250 °C with a 10 °C/min ramping rate and 50 mL/min sample purge flow rate under nitrogen condition. The DSC characterization was conducted to observe if the cleaving reaction occurs up to 250 °C since another limitation of self-healing polymers created using maleimide and furan molecules for the reversible DA reaction is that they contain lower cleaving temperatures (around 120 °C). This is since the polymer could considerably degrade when the polymer is heated above the cleaving reaction through thermally induced cleavage of the DA bonds. The DSC data in Figure 3-5B shows no heat flow transitions as a function of temperatures up to 250 °C, thus indicating the polymers do not experience cleaving reactions below this temperature. These TGA and DSC data demonstrate that the healing response is not a function of thermally induced cleavage, but mechanically induced cleavage of the DA bonds followed by reformation upon application of thermal energy. The healing response may occur at room temperature, which heals micro-cracks and prevents the onset of critical damage. However, under the macroscopic fracture conditions studied here, the crack sterically hinders the reformation of the bond.
Figure 3-5. TGA and DSC curves for thermal analysis. A) TGA curves for decomposition temperatures and B) DSC curves for phase stability up to 250 °C.

3.4.3 Mechanical Properties

The mechanical stability of the self-healing polymers developed under high temperature exposure has been evaluated in order to demonstrate that the polymers do not degrade due to the application of constant heat. Tensile testing and CT testing were conducted to evaluate the properties of the developed polyurethanes$^{53,127}$ and these values were compared to reported commercial epoxy data. In addition, the specimens were heat treated at 160 °C for 20 hours and the heat treated specimens were tested to ensure heat stability as well as heat resistivity. Each test was conducted on four specimens and the average results were reported along with the standard deviations. From the tensile testing, the ultimate tensile strength, strain, and Young’s modulus were obtained and the specimens (based on ASTM 638 Type V) were tested at room temperature with an opening rate of 5 mm/min. For the CT testing, the samples (based on the ASTM D 5045) were prepared and examined at room temperature on an Instron 5936 with an opening rate of 5 mm/min.

Mechanical testing was performed before and after annealing the polymer at 160 °C for 20 hours under a nitrogen atmosphere with the resulting mechanical properties
reported in Table 3–2. The results shown in Table 3–2 verify that the polymer does not degrade under the application of continuous heat and instead, these results indicate that the tensile strength and fracture toughness of the samples improve. The improved strength and toughness may be a result of further crosslinking, increased crystallinity and also the relaxation of internal stresses or micro voids in structures from curing\textsuperscript{128}.

Accordingly, the annealed polymer structure helps to enhance the strength and toughness which are reflected in the mechanical properties. Notably, the polymer exhibits mechanical properties equivalent to aerospace grade epoxies and the previously developed self-healing polyurethane (1.5DA1T) with higher heat resistance. The high mechanical strength, stiffness and toughness of this polyurethane show the polymer can be in applications where temperature environments reach as high as 160 °C without degrading.

Table 3–2. Mechanical properties and standard deviations (SD) of 0.5HTDA1T and 0.8HTDA1T before and after heat treatment (compared to 1.5DA1T and epoxy)

<table>
<thead>
<tr>
<th>Property</th>
<th>0.5HTDA1T (SD)</th>
<th>0.8HTDA1T (SD)</th>
<th>1.5DA1T (SD)</th>
<th>Epoxy</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Before</td>
<td>After</td>
<td>Before</td>
<td>After</td>
</tr>
<tr>
<td>Ultimate tensile strength (MPa)</td>
<td>78.1 (8.0)</td>
<td>85.0 (7.3)</td>
<td>83.0 (4.8)</td>
<td>89.4 (4.7)</td>
</tr>
<tr>
<td>Ultimate tensile strain (%)</td>
<td>11.5 (6.9)</td>
<td>8.6 (3.8)</td>
<td>4.1 (0.7)</td>
<td>5.0 (1.2)</td>
</tr>
<tr>
<td>Young’s modulus (GPa)</td>
<td>2.4 (0.08)</td>
<td>2.5 (0.07)</td>
<td>2.7 (0.06)</td>
<td>2.7 (0.09)</td>
</tr>
<tr>
<td>Glass transition temperature (°C)</td>
<td>49.6 (3.2)</td>
<td>52.3 (2.7)</td>
<td>52.8 (1.4)</td>
<td>64.1 (9.8)</td>
</tr>
<tr>
<td>Fracture toughness (MPa\cdot√m)</td>
<td>1.4 (0.2)</td>
<td>1.7 (0.3)</td>
<td>1.1 (0.05)</td>
<td>1.2 (0.09)</td>
</tr>
</tbody>
</table>

* Heat treatment at 160 °C for 20 hours in an inert condition
3.5 Chapter Summary

In summary, the first high modulus self-healing polymer with temperature stability beyond 240 °C was demonstrated. The thermally stable DA reaction between anthracene and maleimide moieties was used to achieve high temperature stability and thus, the polymers did not exhibit cleaving and thermal degradation until 240 °C. The self-healing behavior was obtained only through the reformation of mechanically cleaved DA adducts rather than thermally reversible DA reactions which place limits on the polymer’s use temperature. Therefore, the crosslinking DA efficiency between these molecules was analyzed and confirmed through the use of VT NMR and then, the thermal stability was investigated through TGA and DSC. The synthesized high temperature stable self-healing polyurethanes (0.5HTDA1T and 0.8HTDA1T) exhibited high average first healing efficiencies of 67% for 0.5HTDA1T and 94% for 0.8HTDA1T. The presented solvent-free polymerization methods where solid anthracene was used as the starting material yielded liquid monomers, thus expanding the application potential for the polymers and greatly simplifying the bulk specimen polymerization process. Additionally, mechanical testing of the polymers demonstrated that the polyurethanes were thermally stable and possessed strength, stiffness and toughness comparable to commercial epoxy.
4.1 Chapter Introduction

Considerable attention has been given to the development of advanced carbon fiber reinforced polymer (CFRP) composites, primarily due to their high specific strength and stiffness\(^5,6,9\). The specific properties of carbon fiber materials are beneficial in many applications since energy efficiency can effectively increase with lighter weight\(^129-131\). Therefore, carbon fiber structural composites are well suited for use in aircraft, automobiles, and high performance sporting goods\(^5-10\). However, CFRP composites are subject to a variety of damage mechanisms that are both difficult to identify and repair. For this reason, one of the biggest challenges to achieving long-term stability with a CFRP composite is the ability to control or to eliminate matrix dominated defects such as micro-cracking and delamination of the plies in the resin rich interlaminar region\(^10,132,133\). As a result, methods to improve the life and durability of self-healing composites have been studied extensively.

Several types of self-healing CFRP composites have been studied since the 1990’s, and the first was developed using healing agents dispersed in capillaries\(^13,62,134\) or micro-capsules\(^59,135-137\). Although these systems often have high healing performance and can trigger the healing response autonomously, the healing function is limited to the amount of embedded healing agent in the composites. Moreover, the healing agent is typically a liquid phase that does not provide reinforcement and voids can be left following rupture of the capillary or capsule, which can subsequently reduce the fracture...
strength of the composite. Blends of thermosetting and thermoplastic polymers have also been used as a self-healing matrix by capitalizing on the thermoplastic phase’s ability to diffuse across a crack upon heating above the melting point\textsuperscript{26,65,66}. Blended polymer matrix systems tend to heal cracks with moderate efficiency and repeatability; however, the thermoplastic typically phase separates and therefore produces either thermoplastic particles or a thermoplastic matrix that can drastically change the material behavior. For instance, if low melting point thermoplastics are used, the hot performance and useful temperature range of the composite can be drastically decreased. If a high temperature engineering thermoplastic polymer such as polysulfone is used, the matrix can experience damage or significant thermal stresses upon heating to induce melting of the polymer. Upon phase separation, poor interfacial adhesion between the thermoset and nonfunctionalized thermoplastics can also occur and negatively affect mechanical properties\textsuperscript{69}. Moreover, undesirable reactions can occur between the blended polymers and the resulting byproducts can cause the formation of internal bubbles on the interface of the two phases when sample temperatures are elevated for healing\textsuperscript{27,28,66}. Finally, intrinsically healable polymers such as those which employ the Diels-Alder (DA) reaction have been embedded as the polymer matrix\textsuperscript{52,70}. The DA reaction is a temperature-dependent, fully reversible reaction between a diene and a dienophile deriving a cyclohexene\textsuperscript{71} and the cyclohexene returns to the diene and the dienophile at higher temperature, called the retro DA (rDA) reaction\textsuperscript{72}. Healing can be obtained with the DA reaction since DA bonds are weaker than other covalent bonds. Therefore, cracks tend to propagate through the DA bonds when excessive loads are applied and these broken DA bonds can become
reconnected at elevated temperatures. Polymers which employ the DA reaction do not autonomously initiate the healing process when cracks occur as in microcapsule and capillary designs; however, healing is intrinsic to the polymer and thus does not leave any voids behind after healing is performed.

Self-healing polyurethanes (1.5DA1T and 2DA1H) using the reversible DA reaction were developed in Chapter 2 with healing efficiencies ranging from 80% to 85% determined using compact tension testing. The differences between these two polyurethanes are due to the varying crosslink densities and molar fractions of DA moieties. When compared to the first polyurethane (1.5DA1T), the second polyurethane (2DA1H) has a higher crosslink density because it was developed by using quadrol to allow a greater molar fraction of DA moieties. Both polyurethanes not only showed excellent healing efficiencies but also have unique aspects compared to other types of self-healing polymers which use the DA reaction. This includes the elimination of external forces during the healing process by taking advantage of the shape memory properties of the polyurethanes. This resulted in heat being the only necessary stimulus needed to close the crack surfaces and reform the broken crosslinks. In Chapter 3, additional self-healing polyurethanes were developed by using an anthracene moiety as the dienophile molecule in order to improve upon the relatively low cleaving temperature (133 °C) of the self-healing polymers presented in Chapter 2. These additional polymers exhibited superior and repeatable healing efficiency as well as excellent heat stabilities up to 240 °C, which can be the maximum useful temperature for applications. However, for these polymers, the shape memory effect was not sufficient enough to eliminate the use of external pressure. For both polymers from Chapter 2 and Chapter 3, the DA and
HTDA moieties were directly linked into the polymer main chain to maintain the mechanical properties of the polyurethanes, resulting in mechanical properties equivalent to, or better than, one of the engineering epoxies. The following discussion shows that the novel self-healing polyurethanes can be employed as the polymer matrix during the fabrication of self-healing CFRP composites. The healing efficiencies of the CFRP composites were characterized using short beam shear (SBS) testing. Then, in order to compare the shear strength of the CFRP composites, carbon fiber reinforced epoxy composites were also fabricated and tested for short beam strength.

4.2 Composite Preparation

4.2.1 Materials

Commercial furfuryl alcohol (FA), triethanolamine (TEA), N,N,N',N'-tetrakis(hydroxypropyl)ethylenediamine (HPED), hexamethylene diisocyanate (HDI) and all chemicals for the N-(2-Hydroxyethyl)-maleimide (HEM) synthesis (maleic anhydride, furan, ethanolamine, methanol, and toluene) were ACS certified grade and used as received. Unidirectional carbon fabric (US Composites, FG-CFU001, as received) was employed as the reinforcement for the composites.

4.2.2 Polymer Syntheses

The first reaction shown in Figure 4-1 was carried out in toluene at room temperature by using the DA reaction to protect the C=C bonds in maleic anhydride with furan since the C=C bonds can be attached by the amine functional group from ethanolamine. The resulting compound (1) was precipitated out at room temperature once the reaction had reached completion and been vacuum filtered. Compound (1) was then reacted with ethanolamine in an ice bath for 30 minutes, followed by refluxing in methanol for 24 hours. Upon completion of the reaction, the mixture was cooled down
to room temperature and the resulting compound (2) was crystallized and vacuum filtered without any further purification process. Then, the furan was removed through the rDA reaction by refluxing the solution in toluene until the peaks for the furan molecule were no longer detected at 6.53 ppm and 5.10 ppm with proton nuclear magnetic resonance (\textsuperscript{1}H NMR). Finally, the solution was cooled down and the HEM was crystallized from the toluene. Additionally, in order to confirm that all DA molecules were crosslinked before testing was performed, the HEM and FA were precrosslinked at 75 °C for 12 hours in toluene. Once the HEM and FA were completely crosslinked, the DA adduct was precipitated out from the toluene solvent at 75 °C, thus the resulting compound could be vacuum filtrated and washed with diethyl ether. Also, HTDA was employed in the polymer (0.8HTDA1T) synthesis process to ensure that all HEM and 9-anthracenemethanol molecules were fully crosslinked before testing. The synthesized HEM and 9-anthracenemethanol were refluxed in toluene for 24 hours. Then, the solution was hot-filtered and cooled down to room temperature in order to produce HTDA as shown in Figure 4-1.

The self-healing polyurethanes which were developed in Chapters 2 and 3 by using these monomers, are employed in this work. The first two composites were fabricated by employing two different polyurethanes (1.5DA1T and 2DA1H) using a precrosslinked DA diol consisting of HEM and FA, the polyols TEA or HPED, and HDI. Then, the second composite was fabricated using one of the high temperature polyurethanes (0.8HTDA1T) that consists of precrosslinked HTDA diol of HEM and 9-anthracenemethanol, TEA, and HDI. HEM was utilized during composite fabrication, and was synthesized through the three step process shown in Figure 4-1. Two different
molar ratios of polyurethanes (1.5DA1T and 2DA1H) were prepared with the synthesized DA, TEA/HPED, and HDI monomers. For 1.5DA1T, 1.5 moles of DA monomer, 1 mole of TEA, and 3 moles of HDI were used. Similarly, 2 moles of DA monomer, 1 mole of HPED, and 4 moles of HDI were used when synthesizing 2DA1H. Another polyurethane (0.8HTDA1T) was also prepared with 0.8 moles of precrosslinked HTDA, 1 mole of TEA, and 2.3 moles of HDI.

Figure 4-1. A schematic of the monomers’ (DA and HTDA) syntheses procedures.

4.2.3 Composite Fabrication

The polyurethanes were infused with the fiber fabrics using vacuum assisted resin transfer molding (VARTM), as shown in Figure 4-2. Three different composites were fabricated and then designated C1.5DA1T, C2DA1H, and C0.8HTDA1T due to the use of 1.5DA1T, 2DA1H, and 0.8HTDA1T, respectively. As verified through nitric acid
digestion according to ASTM D 3171 procedure A, the VARTM method yields high volume fraction composites\textsuperscript{138} (70\% fiber and 30\% resin for C1.5DA1T, 73\% fiber and 27\% resin for C2DA1H, and 71\% fiber and 29\% resin for C0.8GTDA1T by volume). When fabricating samples, 12 plies of unidirectional carbon fiber fabric with dimensions of 25.4 mm x 76.2 mm were used and the thickness of the fabricated composite samples were between 3.3 mm and 3.4 mm.

Figure 4-2. Schematic of vacuum assisted resin transfer molding system. [Reprinted with permission from Heo, Y. & Sodano, H. A. Thermally responsive self-healing composites with continuous carbon fiber reinforcement. *Compos. Sci. Technol.* **118**, 244-250, (2015)]

In order to prepare the molten resins and fabricate the composites, two methods were used due to the different behaviors of DA and HTDA. For 1.5DA1T and 2DA1H, due to the high melting point of the DA monomer, DA and either TEA or HPED were heated and mixed at 105 °C until the DA monomer was melted completely. Next, while stirring, HDI was added to the molten DA mixture at 105 °C. Then, the completely mixed molten resin at 105 °C was added through one tube while vacuum was applied with the other. After the resin was completely transferred, another aluminum plate was placed on top of the VARTM setup in order to press the specimen with a pressure of approximately 100 psi. The specimen was heated at 125 °C for two hours, followed by heating at 90 °C for two hours with final heating at 70 °C for two more hours on a hot press. The temperature profile was designed to stay below the rDA cleaving
temperature (approximately 130 °C) to ensure all the DA bonds in the matrix connected before testing. In order to make sure the resin completely polymerized, the composite was removed from the aluminum plate followed by heating the free standing sample again with the same temperature and time profiles in an oven. For 0.8HTDA1T, 0.8 moles of HTDA and 2.3 moles of HDI were prepolymerized at 105 °C for approximately 3 hours until the mixture became completely transparent. The molten resin was mixed with TEA until it became one phase. Then, similar to the previous method, the molten resin at 105 °C was added through one tube while vacuum was applied with the other. After the resin was completely transferred, another aluminum plate was placed on top of the VARTM setup in order to press the specimen with a pressure of approximately 100 psi. The specimen was heated at 150 °C for three hours on a hot press, followed by heating at 150 °C for two hours in an oven without any pressure to ensure complete polymerization.

When fabricating all the composites, the resin transfer was completed within a short period of time since the molten 1.5DA1T, 2DA1H, and 0.8HTDA1T polymers become highly viscous within the first 30 minutes. Therefore, in order to increase the resin mobility during transfer to the low pressure outlet tube, Teflon film was employed to reduce the friction between the resin and plate and moreover, the VARTM setup as shown in Figure 4-2 was placed on a 60 °C hot plate.

As a comparison, carbon fiber reinforced composites with epoxy (Epon 862 and curing agent 3230) were fabricated with the same VARTM setup in order to compare the short beam strength testing results of C1.5DA1T, C2DA1H, and C0.8HTDA1T with commercially accepted resin. The previous VARTM procedures were followed and a
standard curing temperature profile for Epon 862 with curing agent 3230 was applied. The epoxy specimen were kept at room temperature for 20 hours, heated up to 80 °C for two hours, and then heated up to 125 °C for three hours under a pressure of approximately 100 psi.

4.3 Characterization of Composite Healing Performance

4.3.1 Healing Process

In regards to composite healing procedures, after short beam shear testing, the composite specimens were placed on a hot press and pressed with a pressure of approximately 100 psi, which is the same pressure as the composite fabrication pressure. Then, for C1.5DA1T and C2DA1H, the specimens were heated up to 135 °C for two hours, cooled down and kept at 90 °C for two hours, and then finally lowered and maintained at 70 °C for another two hours. In this process, an additional 15 minutes was allowed for each transition of temperature. The temperature profile was determined in order to allow enough time for the DA and rDA reactions to proceed and this was based on the variable temperature (VT) proton NMR analysis of the DA monomers from Chapter 2. The healing temperature profile was designed to heat the specimens above the cleaving temperature in order to break the crosslinked DA molecules first, so as to enhance the healing ability due to the presence of additional DA reactions between molecules. For C0.8HTDA1T, the specimens were heated from room temperature to 160 °C and then kept at the same temperature for two hours. Then, the specimens were cooled down and kept for two hours at 120 °C, followed by 2 hours at 70 °C under a pressure of 100 psi in a hot press. Between the different temperature conditions, an extra 15 minutes was needed to regulate the set temperatures. The healing temperature profile for C0.8HTDA1T was the same as that for 0.8HTDA1T.
4.3.2 Healing Efficiency

The healing efficiencies of the composite samples were calculated using short beam strength data obtained through short beam shear testing. This testing was performed on an Instron 5969 and the experimental setup is shown in Figure 4-3. The specimen dimensions and testing procedures were provided by the ASTM D2344 standard. According to the standard, for a specimen with a thickness of 3.3 mm, the prepared specimen should have a width of 6.6 mm and a length of 19.8 mm. A total of 13 specimens were initially tested at room temperature at a rate of 1 mm/min. This process was performed twice more on each specimen to obtain first and second healing cycle efficiencies.

Figure 4-3. Short beam shear testing experimental setup. [Photo courtesy of Heo Y. and Sodano H.] [Reprinted with permission from Heo, Y. & Sodano, H. A. Thermally responsive self-healing composites with continuous carbon fiber reinforcement. Compos. Sci. Technol. 118, 244-250, (2015)]
SBS testing was once again conducted to measure the post-healing maximum load. Representative SBS testing results for C1.5DA1T, C2DA1H and C0.8HTDA1T are presented graphically in Figure 4-4A, 4-4B, and 4-4C, respectively. The average healing efficiencies are presented in Table 4-1 and also shown in Figure 4-4D. C1.5DA1T, C2DA1H, and C0.8HTDA1T achieved average efficiencies of 87.8%, 84.7% and 69.1% for the first healing and 72.7%, 73.8%, and 52.4% for the second healing, respectively.

Figure 4-4. Example SBS testing results for a specimen of A) C1.5DA1T, B) C2DA1H, and C) C0.8HTDA1. D) The average healing efficiencies of C1.5DA1T, C2DA1H, and C0.8HTDA1T for the first, and second healing. [Reprinted with permission from Heo, Y. & Sodano, H. A. Thermally responsive self-healing composites with continuous carbon fiber reinforcement. Compos. Sci. Technol. 118, 244-250, (2015)]
Table 4-1. The average healing efficiencies and standard deviations of C1.5DA1T, C2DA1H, and C0.8HTDA1T.

<table>
<thead>
<tr>
<th>Composite</th>
<th>First Healing Efficiency*</th>
<th>Standard Deviation</th>
<th>Second Healing Efficiency*</th>
<th>Standard Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1.5DA1T</td>
<td>87.8%</td>
<td>11.3</td>
<td>72.7%</td>
<td>9.4</td>
</tr>
<tr>
<td>C2DA1H</td>
<td>84.7%</td>
<td>8.4</td>
<td>73.8%</td>
<td>10.5</td>
</tr>
<tr>
<td>C0.8HTDA1T</td>
<td>69.1%</td>
<td>3.7</td>
<td>52.4%</td>
<td>10.6</td>
</tr>
</tbody>
</table>

*Healing efficiency is equal to post-healing maximum load divided by initial maximum load multiplied by 100

After the SBS testing and healing process, the surfaces of the specimens were observed using optical microscopy to visualize the healing performance. Images from an example specimen are shown in Figure 4-5. The SBS testing caused significant delamination throughout the composite (Figure 4-5A) and upon healing; delamination in the composite is effectively eliminated (Figure 4-5B).

Figure 4-5. Optical microscopy images of a composite laminate specimen A) before and B) after healing. Note that the multiple delamination sites produced from the SBS testing are eliminated after healing. Scalebar: 50 μm [Photo courtesy of Heo Y. and Sodano H.][Reprinted with permission from Heo, Y. & Sodano, H. A. Thermally responsive self-healing composites with continuous carbon fiber reinforcement. Compos. Sci. Technol. 118, 244-250, (2015)]

If the average healing efficiencies of the composites (Table 4-1) are compared to the polymers (1.5DA1T and 2DA1H in Table 2-2, and 0.8HTDA1T in Table 3-1), in
general the healing efficiency of all the composites (C1.5DA1T, C2DA1H and C0.8HTDA1T) were marginally lower than those of the polymers (1.5DA1T, 2DA1H, and 0.8HTDA1T). There are several reasons for the different healing efficiencies between the polymers and the composites. In order to investigate the reasons, the damage that resulted from the SBS testing in the composites were identified using a scanning electron microscope (SEM, TESCAN VEGA3 LM). Before testing, the specimens were prepared and polished in order to remove scratches that might cause false defects to be observed. Then, the SBS testing was conducted and images of defects from the surfaces of the specimens were obtained. According to the SEM images, the defects likely occurred in two areas as shown in Figure 4-6, including: (1) through the polymer matrix region (Figure 4-6D) or, (2) on the fiber surface (Figure 4-6B).

![Figure 4-6 SEM images of C0.8HTDA1T showing A) four different damages from SBS testing, B) carbon fiber damage C) delamination between glass fibers and also glass fiber damage, and lastly D) delamination between carbon fibers. Each yellow arrow points out unhealable fiber damage. Scalebar: 50μm. [Photo courtesy of Heo Y. and Sodano H.]](image_url)
Reasons that the healing efficiencies of the composites are lower than that of the polymers include the following. The resulting cracks created through the polymers were healed via the DA reaction; however, in order to completely heal the internal cracks in the composites, the carbon fibers would have needed to remain in their original positions when delaminating. Voids due to misplaced fibers might also form between the crack surfaces during the healing process. Due to the fractured or damaged reinforcing fibers which cannot be healed, the composites have reduced strength upon retesting.

The average short beam strengths from 13 specimens of each unidirectional carbon fiber reinforced composites (C1.5DA1T, C2DA1H, and C0.8HTDA1T), and the epoxy composites fabricated with Epon 862 and curing agent 3230 were determined to be 44.7 MPa, 55.7 MPa, 69.1 MPa, and 65.2 MPa, respectively. Although the average shear strengths of C1.5DA1T and C2DA1H were not greater than the tested epoxy composite, they are higher than the values reported by Gong for the CFRPs fabricated with commercial diene and dienophile monomers, poly(furfuryl alcohol) and 4,4’-bismaleimidodiphenylmethane, and also for the CFRP fabricated with Chen’s DA monomer, 2MEP4F\textsuperscript{94}. These observed strengths were possible since the self-healing moieties were attached to the polyurethane backbone and the mechanical properties of polyurethane were maintained in the composites.

Unlike the polymers that were able to heal with only the shape memory effect, the self-healing composites using the DA reaction were not able to recover their short beam properties without the use of external forces. Originally, the specimens were heated in an oven without any applied force, which allows plastic deformation in bent
specimens after short beam testing to recover their shape through heating. However, the SBS testing showed that the slope was much smaller than the initial curve, meaning that crack defects were not healed. This is most likely because the shape memory recovery force is not large enough to shift the delaminated fabric. Also, if any of the fibers shifted into a different position when delaminating, even greater pressures would be needed to force the cracked surfaces back into contact. It may be possible to use the shape memory properties for healing without the application of an external force in larger specimens with a greater volume of undamaged polymer and fiber. The results presented here demonstrate a high strength carbon fiber reinforced polymer that exhibits repeatable healing. Furthermore the self-healing polymers were processed through typical commercial resin infusion processes, thus allowing them to be applied in the manufacture of composites with both shape and strength recovery.

4.4 Chapter Summary

In summary, CFRP composites were developed by using a thermo-responsive self-healing polyurethane matrix where the healing was accomplished through the DA reaction. These CFRP composites (C1.5DA1T, C2DA1H and C0.8HTDA1T) were fabricated with the VARTM method and by using two different self-healing polyurethanes from Chapter 2 and one polyurethane from Chapter 3. Then, the healing efficiency and shear strength of each composite was tested for accordingly. By conducting SBS testing and using the maximum loads, the average healing efficiencies were shown to be roughly 88% for C1.5DA1T, 85% for C2DA1H, and 67% for C0.8HTDA1T during the first healing cycle; subsequent damage was also repeatedly healed. The thermally responsive, self-healing composites were also shown to have
excellent mechanical properties, and tests showed comparable short beam strength to that of similar commercial composites which utilize epoxy as the polymer matrix.
CHAPTER 5
CONCLUSIONS

In this work, self-healing polymers and carbon fiber reinforced polymer (CFRP) composites have been investigated and characterized through various methods and testing. Intrinsically healable polymers were first studied, followed by self-healing CFRP composites which were fabricated using the healable polymer resins as a matrix.

For all the developed polymers, the Diels-Alder (DA) reaction was employed for the healing mechanism and a polyurethane network was chosen in order to retain stability and superior mechanical properties. First, three new thermo-responsive self-healing polyurethanes (1DA1T, 1.5DA1T, and 2DA1H) based on the DA reaction between maleimide and furan moieties were developed. Unlike other self-healing polymers seen in the literature, these polymers do not require external forces to close cracks but rather they use the shape memory effect to bring the crack faces into intimate contact to initiate autonomous healing. In order to verify the transition temperatures of the polymers (i.e., the glass transition temperature and the DA and retro Diels-Alder (rDA) reaction temperatures), a differential scanning calorimeter was used. Additionally, in order to confirm the repeatability of the DA and rDA reactions, variable temperature nuclear magnetic resonance (VT NMR) was utilized. Healing efficiency was calculated by using the initial and post-healing maximum loads that were acquired through the use of compact tension (CT) testing. The results showed that the shape memory recovery force can replace external pressure to close two crack surfaces and that the DA reaction can be repeatedly employed to heal the cracks.

In order to resolve the limitation of a relatively low cleaving temperature seen with the first group of polymers, further investigation into self-healing polymers
synthesized through the reaction between maleimide and anthracene moieties was conducted. As a result, two additional novel self-healing polyurethanes (0.5HTDA1T and 0.8HTDA1T) were created with cleaving temperatures higher than the polymer’s decomposition temperature (approximately 250 °C). This was verified through differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA), and results indicated that only crosslinking DA reaction could also be employed for the healing process. The efficiency of the DA reaction between maleimide and anthracene was characterized by VT NMR. Also, the healing efficiencies of these two polymers were calculated based on data from CT testing.

CFRP composites (C1.5DA1T, C2DA1H and C0.8HTDA1T) were fabricated by using the self-healing polyurethanes (1.5DA1T, 2DA1H and 0.8HTDA1T) as a matrix in order to demonstrate that intrinsic healing properties of resins can be maintained in composites without any treatment of the carbon fiber. To evaluate the healing efficiencies of these composites, short beam shear testing (which generates delamination inside the composite panels) was conducted. The results of the testing show that the composites are stable and that they can be repeatedly healed.

5.1 Summary of Dissertation

The first part of this work (Chapter 2) demonstrated that polymers combining two functionalities (self-healing and shape memory) can be developed. These functionalities eliminate the need to apply an external force to close a crack during the healing process. Also, by linking the DA moieties into the polymer main chains, the developed polyurethanes retained excellent mechanical properties comparable to epoxy. The transition temperatures for the DA and rDA reactions between N-(2-Hydroxyethyl)-maleimide (HEM) and furfuryl alcohol (FA) molecules were analyzed
through DSC. The crosslinking transition temperatures were an average of 97 °C for 1DA1T, 97 °C for 1.5DA1T, and 96 °C for 2DA1H. The cleaving transition temperatures were an average of 132 °C for 1DA1T, 129 °C for 1.5DA1T, and 130 °C for 2DA1H. These results indicated that the DA and rDA reactions occurred around the same temperature, even when different molar ratios of monomers were used to synthesize the polymers. Repeatability of the DA and rDA reactions were verified through both proton and carbon VT NMR analyses. Two proton peaks at 5.08 ppm and 6.52 ppm and also two carbon peaks at 91.8 ppm and 80.5 ppm were observed, indicating that the protons and carbons of the newly formed σ C-C bonds appeared after crosslinking at 80 °C and disappeared after cleaving at 140 °C. From these results, it could be concluded that the reactions are repeatable for multiple times. Finally, the healing efficiencies calculated using maximum fracture loads from CT testing confirmed the repeatable healing. The healing efficiencies of 80%, 84%, and 96% were calculated for the first healing cycle for 1DA1T, 1.5DA1T and 2DA1H, respectively, and only a slight loss in healing efficiencies were seen with each subsequent cycle.

The thermally reversible form of the DA reaction placed a limitation on the temperature range for which these polymers can be used. Hence, the DA reaction between anthracene and maleimide moieties was investigated for the healing mechanism in Chapter 3. For these self-healing polymers (0.5HTDA1T and 0.8HTDA1T), similar to the initially developed polymers (1DA1T, 1.5DA1T, and 2DA1H), a polyurethane network was used and the DA moieties were directly connected to the polymer’s main chain for superior mechanical properties. In order to confirm a thermal stability of up to 250 °C, DSC and TGA were conducted. From the DSC results, it could
be concluded that the polymers do not experience cleaving reactions below 250 °C. The TGA data indicated that the polymers were stable up to 251 °C for 0.5HTDA1T and 240 °C for 0.8HTDA1T. These data are significant since it has been shown that these polymers can be used in applications that require thermal stability up to 240 °C. Moreover, the efficiencies of the crosslinking reactions were analyzed in solvent with VT $^1$H NMR and the reactions proceeded to roughly 100% completion within 15 minutes at 140 °C. Then, the healing efficiencies were calculated using CT fracture testing and values of 66% for 0.5HTDA1T and 94% for 0.8HTDA1T were obtained for the first healing cycle. Hence, this work (Chapter 3) shows that the repeatable self-healing behavior could be obtained purely through the reformation of mechanically cleaved DA adducts. The reported self-healing polymers were also synthesized from liquid monomers, allowing the polymerization of bulk samples that yield mechanical properties (i.e., strength, stiffness and toughness) comparable to other engineering polymers. However, these polymers needed to be compressed by external forces during the healing process in order to obtain the healing performance, unlike the initially investigated polymers (1DA1T, 1.5DA1T, and 2DA1H).

Finally, as shown in Chapter 4, carbon fiber-reinforced polymer composites (C1.5DA1T, C2DA1H, and C0.8HTDA1T) were fabricated by using two different self-healing polyurethanes from Chapter 2 and one polyurethane with the high temperature stability from Chapter 3$^{139}$. CFRP composites were fabricated though resin infusion of the self-healing polymers and were tested via short beam shear testing. The composites achieved high healing efficiencies of 88% for C1.5DA1T, 85% for C2DA1H, and 67% for C0.8HTDA1T during the first healing cycle and 73% for C1.5DA1T, 74% for C2DA1H,
and 52% for C0.8HTDA1T during the second cycle. These results show that subsequent damage could also be healed; however, the usage of external forces was required since the shape memory force from approximately 30% by volume of matrix was not sufficient enough to bring the shifted fibers back to their original locations. The thermally responsive, self-healing composites were also shown to have excellent mechanical properties, including averaged shear strengths of 44.7 MPa, 55.7 MPa, and 69.1 MPa for C1.5DA1T, C2DA1H, and C0.8HTDA1T, respectively. These values were comparable to the reported shear strength of 65.2 MPa for composites fabricated with epoxy (Epon 862 and curing agent 3230) as the polymer matrix.

5.2 Contributions

By fabricating and then characterizing novel self-healing polymers and CFRP composites, numerous contributions have been made to the existing body of knowledge concerning these topics. These contributions include the following:

- The idea of the usage of shape memory recovery force from the self-healing polymer itself to close crack surfaces was introduced.
- Adaptable, inexpensive maleimide moiety synthesis was explored.
- DA healing molecules were directly connected into a polymer’s main chain.
- Self-healing polymers with excellent mechanical properties comparable to commercial epoxy were obtained.
- Bulk specimens by solvent-free polymerization methods were successfully synthesized.
- The repeatability and efficiency of the DA and the rDA reactions at the actual reaction temperatures were analyzed by using VT NMR.
- Demonstrated that composites are able to be self-healing with only the incorporation of a healable resin as the matrix.
5.3 Recommendations for Future Work

A number of novel methods in which to synthesize and characterize the properties of self-healing materials were developed during the course of this research. Even though the developed self-healing polymers and composites obtained repeatable healing performances as well as superior mechanical properties, there are still some drawbacks to these materials that can be improved upon. Furthermore, additional approaches to analyze the properties of these materials can be considered to further understand the mechanisms and systems.

In this work, the shape memory recovery force was introduced to eliminate the use of external forces to close cracks. This allows the materials to require only one thermal stimulus to initiate healing since a second external pressure stimulus can be replaced during the healing process. However, the requirement of using an external force during the healing process was only successfully eliminated when the polymers were synthesized using maleimide and furan moieties (1DA1T, 1.5DA1T, and 2DA1H). For the other polyurethanes (0.5HTDA1T and 0.8HTDA1T) and all the CFRP composites, an external force was still required. Hence, in the future it would be beneficial to quantify the minimum recovery force that is required in order to eliminate the necessity of external forces in these other polyurethanes and CFRP composites.

Self-healing polyurethanes with maleimide, furan and anthracene were developed and the results showed that the polymers could be repeatedly healed with excellent healing efficiencies, but this work is by no means complete. The first drawback noticed after the work for Chapter 2 was completed, was the relatively low cleaving temperature of 133 °C between the maleimide and furan moieties. This could limit the use of higher temperature required applications because the reverse reaction can affect
the stability of the polymers. Therefore, as presented in Chapter 3, anthracene was successfully employed instead of furan and the results demonstrated that the cleaving temperature of polymers could be increased to higher than 250 °C. However, the DA reaction between anthracene and maleimide should be reversible based on theoretical knowledge but the actual temperature range for where this occurs has not yet been determined in an experimental setting since the actual cleaving temperature is very high and the materials decompose before cleaving occurs. Thus, the cleaving transition between anthracene and maleimide moieties was never been able to be characterized in this work or by others in the literature. Therefore, a quantitative analysis of the cleaving temperatures between these two molecules would be very beneficial. This is because it is believed that separation of unbroken bonds into two molecules through the cleaving reaction is still helpful to enhance the repeatable healing ability. Hence, synthesizing a polymer with high temperature stability above at least 300 °C could be one possible approach to observe the actual cleaving transition before decomposition of the polymer. Another drawback of all the developed polymers is that they possess low glass transition temperatures below 80 °C, although they are thermally stable up to 240 °C. A polymer with a low glass transition can have limited use in numerous structural applications. Therefore, the investigation of new DA self-healing polymers that have higher glass transition temperatures is recommended.

Polyurethane was selected as the polymer network due to superior mechanical properties. The main goal of this polymerization work was to include the healable molecules with reversible bonds directly into the polymer’s chains instead of simply mixing the healable agents into the polymer network. This concept was the most
important aspect when developing the new polymers in order to obtain stable and uniform properties throughout the polymers. The disadvantage is that polyurethane is moisture sensitive, meaning that a glovebox was required during monomer preparation and a nitrogen atmosphere was required during polymerization. Using this equipment is not a major limitation for research purposes, but such synthesis requirements could be drawbacks for industrial manufacturing. Therefore, the development of another intrinsic polymer network which can be synthesized in ambient conditions is recommended.
APPENDIX
NUCLEAR MAGNETIC RESONANCE (NMR) SPECTRUMS

4,10-Dioxatricyclo[5.2.1.0^2,6^]dec-8-ene-3,5-dione (1)

Figure A-1. A proton NMR spectrum for product 1 (300 Hz, DMSO-d$_6$, δ 6.59 (s, 2H), 5.36 (s, 2H), 3.32 (s, 2H) ppm)
Figure A-2. A carbon NMR spectrum for product 1 (300 Hz, DMSO-d$_6$, $\delta$ 171.98, 137.30, 82.11, 49.53 ppm)
Figure A-3. A proton NMR spectrum for product 2 (300 Hz, DMSO-$d_6$, $\delta$ 6.53 (s, 2H), 5.10 (s, 2H), 4.74 (br, 1H), 3.40 (br, 4H), 2.90 (s, 2H) ppm)
Figure A-4. A carbon NMR spectrum for product 2 (300 Hz, DMSO-\textit{d}_6, \delta 176.93, 136.89, 80.73, 57.73, 47.57, 41.06 ppm)
N-(2-Hydroxyethyl)-maleimide (HEM)

Figure A-5. A proton NMR spectrum for HEM (300 Hz, DMSO-d$_6$, $\delta$ 6.97 (s, 2H), 4.80 (br, 1H), 3.44 (br, 4H) ppm)
Figure A-6. A carbon NMR spectrum for HEM (300 Hz, DMSO-d$_6$, $\delta$ 171.53, 134.88, 58.37, 40.38 ppm)
Pre-crosslinking DA Adducts (DA)

Figure A-7. A proton NMR spectrum for DA (300 Hz, DMSO-d<sub>6</sub>, δ 6.52 (br, 2H), 5.07 (s, 1H), 4.92 (br, 1H), 4.75 (br, 1H), 4.01 (d, 1H), 3.71 (d, 1H), 3.41 (s, 4H), 3.03 (d, 1H), 2.89 (d, 1H) ppm)
Figure A-8. A carbon NMR spectrum for DA (300 Hz, DMSO-d$_6$, δ 176.85, 175.40, 138.53, 136.91, 92.07, 80.63, 59.40, 57.74, 50.39, 48.21, 41.00 ppm)
Pre-Crosslinked Compounds (HTDA)

Figure A-9. A proton NMR spectrum for HTDA (300 Hz, DMSO-d$_6$, $\delta$ 7.74 (d, 1H), 7.44 (d, 1H), 7.19 (m, 6H), 5.40 (t, 1H), 4.91 (q, 2H), 4.74 (d, 1H), 4.68 (t, 1H), 3.29 (m, 2H), 3.08 (t, 2H), 2.66 (m, 2H) ppm)
Figure A-10. A carbon NMR spectrum for HTDA (300 Hz, DMSO-d$_6$, $\delta$ 177.0, 176.2, 143.0, 140.4, 139.9, 126.8, 126.6, 126.3, 125.2, 124.9, 124.1, 122.9, 58.7, 57.0, 49.8, 48.0, 45.9, 45.5 ppm)
LIST OF REFERENCES


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BIOGRAPHICAL SKETCH

Yunseon Heo was born in 1986 in Cheongju, South Korea. After graduating from Sangdang High School in February 2005, she began studying materials science and engineering at Ajou University in Suwon, South Korea in March 2005. In the fall semester of 2008, she studied abroad at Jönköping University in Sweden as an exchange student in the mechanical engineering department. She then resumed her studies at Ajou University before attending the Illinois Institute of Technology in Chicago, Illinois in December 2009 through a dual degree program. She earned a Bachelor of Science in materials science and engineering at Ajou University in August 2010 and later completed a second Bachelor of Science degree at the Illinois Institute of Technology in May 2011. After receiving both undergraduate degrees, she attended the University of Florida for graduate school in August 2011 and started to work in October 2011 with Dr. Henry A. Sodano on research related to shape memory self-healing polymers. Along the way, she earned her Master of Science in materials science and engineering in December 2013. She expanded her research to include both the development of self-healing polymers and composites for her Doctor of Philosophy degree. She defended her dissertation in the fall of 2015 and looks forward to pushing the boundaries of self-healing materials.