Molecular Level Design of Self-Healing Polyurethanes

Ying Yang
Clemson University

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MOLECULAR LEVEL DESIGN OF SELF-HEALING POLYURETHANES

A Dissertation
Presented to
the Graduate School of
Clemson University

In Partial Fulfillment
of the Requirements for the Degree
Doctor of Philosophy
Materials Science and Engineering

by
Ying Yang
August 2016

Accepted by:
Dr. Marek Urban, Committee Chair
Dr. Philip Brown
Dr. Douglas Hirt
Dr. Igor Luzinov
ABSTRACT

Self-healing synthetic materials emerged a couple of decades ago and continue to attract scientific community driven by the opportunity to develop life-like materials and sustainable technology. Inspired by living organisms which utilize metabolic processes to achieve adaptive, reproductive, and self-healing functions, self-healing synthetic materials require dynamic and precise control of sequential chemical and physical events similar to biological systems. The study presented in this dissertation is inspired by the role of carbohydrates in biological systems as energy storage molecules and structural components. The objective is to obtain self-healing by incorporating carbohydrate molecules into crosslinked polyurethane networks with sophisticated network design, and study the self-healing mechanisms from both chemical and physical perspective.

Two self-healing systems were developed containing carbohydrate molecules, such as methyl-α-D-glucopyranoside (MGP), that are crosslinked into polyurethane (PUR) networks. When network formation is catalyzed by dibutyltin dilaurate (DBTDL), these materials are capable of self-repairing in air by reacting with atmospheric amounts of CO\textsubscript{2} and H\textsubscript{2}O, thus resembling plant’s behavior of carbon fixation during photosynthesis cycle. However, when organotin catalyst was replaced by zinc acetate (Zn(OAc)\textsubscript{2}), similar network composed MGP and PUR exhibited completely different self-healing behavior and chemical re-bonding mechanism. Self-healing proceeds at elevated temperatures, is independent of CO\textsubscript{2} or H\textsubscript{2}O, and is attributed to reaction of damage-induced amines to reform covalent linkages.
As stated earlier, self-healing synthetic materials require dynamic and precise control of sequential chemical and physical events. Therefore, the physical driving force for self-healing was also explored by mechanical analysis and thermodynamic studies. A three-step process is proposed which can lead to self-healing of polymers: 1) shape memory effect induced damage closure, which generates interfacial contacts; 2) chain rearrangements within the interface along with 3) subsequent covalent bond reformation lead to recovery of mechanical strength.

Using the three-step self-healing concept as a platform, a multi-functional material encoded with color change, shape memory, and self-healing attributes in one is designed and synthesized. Phase-separated morphologies are achieved by a chemical makeup and directional drawing that lead to fibrous morphologies of polycaprolactone and polyurethane. The built-in heterogeneity and interphase structure are critical in achieving enhanced shape memory and self-healing attributes.
DEDICATION

I dedicate my dissertation to my mother and father who have been giving me their love, wisdom, guidance, and always the strongest support for all these years. Also to my grandparents, my aunts and uncles, and my cousins who always gave me the heartiest welcome every time I visited home.

I would also like to dedicate this work to my lifelong friends, Yuan Li, Guancheng Gu, Chen Liu, and Yang Song. Thank you for your companion in the past three years at Clemson, which made my everyday life cheerful. Also to my friends, Xiaole Cheng and Xin Jin, for the years we spent in Hattiesburg and all the good memories we have.
ACKNOWLEDGMENTS

I would like to give this special thank you to my advisor, Dr. Marek W. Urban, for the best education I can possibly get as a graduate student. Thank you for having faith in me, and spent countless time in the past five years teaching me with research, writing, communication and presentation skills, critical thinking, and many more. I am also thankful to my research committee: Dr. Philip Brown, Dr. Igor Luzinov, and Dr. Douglus Hirt, for your time and expertise.

I would like to give my appreciation to the faculty and stuff from the School of Materials Science and Engineering and Advanced Materials Research Labs for your support. Thank you in particular to Dr. Igor Luzinov and Dr. Fei Peng for the good experience I had in your classes. Thank you to Kim Ivy and James Lowe for your time and patience helping me with mechanical analysis. I also would like to thank the faculties in School of Polymers and High Performance Materials in University of Southern Mississippi where I spent my first two and a half years, for guiding me into the world of polymers.

Many thanks to my labmates and friends, Chunliang Lu, Zhanhua Wang, Christophor Hornat, Dimitriy Davidovich, and Laura Smith. The time we worked together as a group, the way we trust and respect each other, and all the inspirations, encouragements, and support you guys gave me, are precious. I hope you all the best in your future.
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INTRODUCTION

Living organisms are able to recover from injuries to resume active and reproductive functions. The ability to continue these metabolic processes determines the longevity of their existence. Synthetic materials are designed to be functional, but do not possess metabolic attributes. Driven by an opportunity to develop life-like materials and sustainable technologies, the concept of self-repairing has been explored and became the central topic of scientific interests and technological significance. Although numerous successful approaches have been explored over the last decade, the challenge lies in molecular level design of the material to achieve self-healing as well as desirable chemical and physical properties, and understanding of the self-healing mechanism. The objectives of this dissertation are:

- Design and synthesis of thermosetting and thermoplastic polyurethanes that exhibit self-healing attributes by incorporating dynamic groups into polymer backbones while maintaining mechanical properties.
- Study of the self-healing chemistry by in-situ measurement of chemical environmental changes localized within damaged sites during damage-repair cycles utilizing vibrational spectroscopy.
- Understanding of the physical processes governing the self-healing behavior and illustrate how physical and chemical events are orchestrated leading to network remodel.

The study presented in this dissertation is inspired by the role of carbohydrates in biological systems as energy storage molecules and structural components. It shows that by incorporating carbohydrate molecules into crosslinked polyurethane networks with
sophisticated network design, self-healing can be achieved. In depth study of the self-healing mechanisms are performed from both chemical and physical perspective.

Chapter 1 reviews recent advances in the field of self-healing polymers. The first part focuses on chemical reactions that lead to self-healing, and the primary classes are the reversible covalent bonding and supramolecular assemblies. The second part outlines recent advances using encapsulation, remote self-healing and the role of shape memory polymers. Recent developments in the field of self-healing polymers undeniably indicate that the main challenge will be the designing of high glass transition (T_g) functional materials, which also exhibit stimuli-responsive attributes. Built-in controllable hierarchical heterogeneities capable of remote self-healing capable of physical and chemical responses will be essential in designing future materials of the 21st Century.

Chapter 2 and 3 present two self-healing systems that are developed containing carbohydrate molecules, such as methyl-α-D-glucopyranoside (MGP), crosslinked into polyurethane networks by reacting with hexamethylene diisocyanate trimer (HDI) and polyethylene glycol (PEG). Chapter 2 shows that when network formation is catalyzed by dibutyltin dilaurate (DBTDL), these materials are capable of self-repairing in air by reacting with atmospheric amounts of CO_2 and H_2O, thus resembling plant’s behavior of carbon fixation during photosynthesis cycle. However, when organotin catalyst is replaced by zinc acetate (Zn(OAc)_2), a similar network composed MGP and PUR exhibit completely different self-healing behavior and chemical re-bonding mechanisms. This study is presented in Chapter 3. Self-healing proceeds at elevated temperatures, is independent of CO_2 or H_2O, and is attributed to reaction of damage-induced amines to
reform covalent linkages. These studies not only illustrate the unique chemistries of carbohydrates when incorporated into polyurethanes, but also demonstrate the critical role of the catalysts in polymeric materials although present in minute amount.

As stated earlier, self-healing synthetic materials require dynamic and precise control of sequential chemical and physical events. Therefore, it is also critical to understand the physical driving force for self-healing. Chapter 4 demonstrates the role of shape memory effects in macroscopic damage closure and generating interfacial contacts between damaged surfaces. This process enables subsequent chemical rebonding at the interface of damage. Because shape recovery occurs within rubbery region, self-healing occurs without melting or reshaping the material. Meanwhile, since the polymer matrix that serves the purpose of shape memory driven self-repair is desirable, a new method to assessment of shape memory properties is introduced. Chapter 5 takes this concept further and shows a self-healing lattice model, which describes how thermodynamics of the cleaved chains within the damaged interface contribute to chain rearrangements and self-healing. At this point, a three step self-healing is introduced: 1) shape memory effect induced damage closure, which generates interfacial contacts; 2) chain rearrangements within the interface along with 3) subsequent covalent bond reformations lead to recovery of mechanical strength.

With the knowledge gained in chapters 2 to 5 and the three step-self-healing models, a multi-functional material encoded with color change, shape memory, and self-healing attributes in one is designed and presented in Chapter 6. In this chapter, a heterogeneous polymer that exhibit phase separated morphologies achieved by a
chemical makeup and directional drawing that lead to fibrous morphologies of polycaprolactone and polyurethane is developed. While melting and recrystallization of the PCL domain is responsible for binding the separated chains together, the built-in heterogeneity and interphase structure are critical in achieving enhanced shape memory and chain diffusivity at the interface, thus lead to self-healing attributes. This study not only validates the three-step self-healing model, but also shows that molecular design and material processing together will lead to advanced material properties.
CHAPTER 1 INTRODUCTION TO SELF-HEALING POLYMERS

1.1 Background

Developments of advanced materials have paved the evolution of technologies for the last 50 years and their importance in the advancement of global growth is essential. It is undeniable that since the 1980s, technological changes and economic progress is owned to the development of advanced materials. The recent decades brought about new dimensions to materials developments: stimuli-response materials capable of responding to internal or external stimuli.[1] Although unquestionably these venues formulated the basis of the 21st Century materials and beyond, there are fascinating challenges as well as unprecedented opportunities. While the property-driven view of structures and processes for the creation of value will continue in a commodity research, modern sciences and materials engineering share the view that a new generation of advanced stimuli-responsive materials will fuel energy, world security, and human welfare. One can envision an array of technologies that may capitalize on various stimuli-responsive attributes ranging from sensing to adaptive behaviors and many more, but perhaps that the most promising property is the ability of materials to autonomously self-heal.

If biological systems are used as the benchmark of regeneration, self-healing, and reproduction, mimicking these processes is not trivial because they exhibit highly coordinated and complex cellular and molecular level metabolic activities, enabling coordination of defense responses by assembly-disassembly of heterogeneous morphologies.[2-4] Consequently, designing self-healing processes in materials by even
well-established synthetic paths is a challenge; especially, that very minute side products and side reactions may adversely impact main reaction paths.

Traditional approaches to repair mechanically damaged materials are gluing and patching. As early as 1980s, it was discovered that selected ionomers, such as poly(ethylene-co-methacrylic acid), are able to repair themselves after projectile puncture.[5] A physical model describing a self-healing process was proposed and included five-stage process: segmental surface rearrangements, surface approach, wetting, diffusion, and randomization.[6] In essence, chain diffusion at the polymer-polymer interface was considered as the primary driving force for repairs, and the reptation model semi-quantified these events. Two decades later, self-healing materials once again gained tremendous attentions when embedded hollow fibers, microcapsules, and microvascular networks containing reactive monomers were incorporated into polymer matrix to obtain self-healing.[7] When damage of the polymer matrix occurs, reactive chemicals then “spill” from damaged hollow fibers or microcapsules and crosslink, thus serving as internal glue.

Over the last decade, enthusiasm for self-healing materials continued, and several studies focused on integrating self-healing components into polymer backbones utilizing reversible breaking and reforming of dynamic covalent[8-15] or non-covalent bonds[5, 16-21] induced by temperature, electromagnetic radiation, and/or changes of chemical surroundings (pH, ionic strength, concentrations, and redox reactions). A general damage-repair cycle in these polymers is depicted in Figure 1.1. As shown, mechanical damage of polymer networks will lead to chain cleavage and/or slippage, and subsequent
formation of reactive groups which may or may not proceed conformational changes in a wound area. The reactivity of these groups determines if these entities are able to react with the surroundings to form more stable oxidative products, or will autonomously reassemble to repair damaged area. Thus, the stability of reactive groups resulting from localized chain cleavage will be one of the key features for repairs. At the same time, cleaved and/or displaced macromolecular segments will experience segmental rearrangements resulting in conformational changes or diffusion leading to macroscopic network rearrangements. If these chemico-physical processes are independent of each other or not spatially synchronized, chemical reactions leading to bond reformation will unlikely lead to self-healing, and the same is applicable to physical changes. Thus, interplay between chemical reactions and physical network remodeling is essential if idealized evolution of damage-repair events shown in Figure 1.1 ought to occur.

Figure 1.1. A schematic diagram depicting the evolution of an ideal damage-repair cycle in polymeric materials. Upon mechanical damage, cleavage of macromolecular chains
leads to the formation of reactive end groups, which may be free radicals and/or -C=C-, -COOH, -NH₂, -OH, -Si-O, SH/S-S, or -C=O. If segmental chain mobility and/or diffusion brings reactive groups in contact with each other, bond reformation and physical network repair occur. The recoupling self-healing lattice consists of n self-avoiding walk polymer chains; each chain occupies N lattice segments with coordination number z.

1.2 Self-Healing Chemistries in Polymers

The last decade resulted in the development of a few classes of reactions to offer self-healing through the cleavage and reformation of specific bonds, and are typically categorized into reversible covalent and non-covalent bonds. Using these entities, a significant number of synthetic efforts leading to self-healing networks have been developed, which will be introduced in this section.

1.2.1 Reversible covalent bonds

Dissociation and association rates of the dynamic bonds as well as chain mobility are significant factors in designing self-repairing materials. Reversible covalent bonds are good candidates for developing self-healing polymers due to their high bonding strength, which enhance the mechanical toughness of materials. Four types of self-repairing covalent bonds have been utilized: (1) reversible cycloaddition reactions, (2) exchange reactions, (3) stable free radical mediated reshuffling reactions, and (4) heterocyclic compounds/carbohydrates facilitated bond reformations.

Due to their adaptability to various polymers, Diels-Alder (DA) and similar cycloaddition reactions have been extensively investigated. Adduct (exo or endo)
formation via DA reaction between furan (diene) and maleimide (dienophile) entities can be utilized to build the crosslinked polymer network.[8, 22] Retro-DA reactions, typically induced by elevated temperature and/or crack, result in the disconnection of diene and dienophile, and lower temperatures reconstruct the covalent bonds to repair damages. DA pairs have been incorporated in polyesters, epoxies, and polyamides,[23-26] leading to the formation of self-healing networks with various properties. This is summarized in Table 1.1, A. One drawback of covalent self-healing bonds is the high activation energy, where activation temperature of the retro-DA reaction responsible for the self-healing can be up to 120 °C.[8] The advantage is that T_g of the polymer can be as high as 100 °C, but high temperature exposure may not be desirable (Table 1.1, A, a-c). Ideally, bond dissociation and reformation should proceed at ambient conditions. However, DA pairs that are reversible within mild temperature range are rare and require elaborate synthesis, which compromise the practicality. A novel DA system consisting of cyanodithioester (CDTE) compound and cyclopentadiene (Cp), as shown in Table 1.1, B, was developed to overcome the limitation of slow self-healing kinetics of the previous systems. [27] Crosslinked network formed between CDTE based tetra-crosslinker and linear poly(iBoA-nBA) end capped with Cp groups offer rapid reversibility and self-healing between 70-120 °C without any catalyst.
Table 1.1. Cycloaddition reactions responsible for self-repair. The corresponding physical properties and self-repair conditions are listed for corresponding polymer matrices.

<table>
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<tr>
<th>Self-repair bonds</th>
<th>Matrix/Building Block</th>
<th>Phase Separation</th>
<th>T&lt;sub&gt;g&lt;/sub&gt; (°C)</th>
<th>Moduli</th>
<th>Repair conditions</th>
<th>Recovery (%)</th>
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<tr>
<td>b. Thermosetting epoxy[18]</td>
<td>NA</td>
<td>61</td>
<td>NA</td>
<td>140 °C 30 min and 75 °C 5h</td>
<td>Scratch disappear</td>
<td></td>
</tr>
<tr>
<td>c. Polyester containing furan[19]</td>
<td>NA</td>
<td>7.8 – 8.9</td>
<td>0.014 – 0.213 GPa</td>
<td>rt 5 d</td>
<td>71.9-16.8</td>
<td></td>
</tr>
<tr>
<td>d. Polyamide [20]</td>
<td>NA</td>
<td>250</td>
<td>0.566 GPa</td>
<td>120 °C 3 h and 50 °C 5 d</td>
<td>Scratch partially repaired</td>
<td></td>
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<tr>
<td>e. PEO-b-PFGE block copolymer[21]</td>
<td>19 nm lamella</td>
<td>-40 (-79)</td>
<td>5.13 GPa</td>
<td>155 °C 3 h and 65 °C 14 h</td>
<td>Scratch disappear</td>
<td></td>
</tr>
<tr>
<td>B - Thermal DA reactions between cyanodithioester and cyclopentadiene</td>
<td>Poly(bBoA-nBA) containing cyclopentadiene end groups[22]</td>
<td>NA</td>
<td>31</td>
<td>6.3 MPa***</td>
<td>120 °C 1kN for 10 min</td>
<td>&gt;100</td>
</tr>
<tr>
<td>C - Cinnamoy [2+2] cycloaddition</td>
<td>TCE[23]</td>
<td>Rigid material</td>
<td>42.1 MPa</td>
<td>280 nm UV 10 min</td>
<td>6.4</td>
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<tr>
<td>D - Coumarin [2+2] cycloaddition</td>
<td>Polyurethane with high Mw PEG (Mw 800 g/mol)[24]</td>
<td>Yes (domain size NA)</td>
<td>43.7 (-24.9)</td>
<td>3.5 MPa</td>
<td>254 and 350 nm UV lights 90 min</td>
<td>68</td>
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*: Yong’s modulus; **: flexural strength; ***: tensile strength, rt – room temperature.
In order for materials to self-repair without excessive heating, photochemical cycloadditions provide an optically induced self-healing process. These include [2+2] cycloaddition of 1,1,1-tris-(cinnamoyloxy-methyl)ethane (TCE) (Table 1.1, C) [28] or coumarin (Table 1.1, D), [29] and [4+4] cycloaddition of anthracene derivatives (Table 1.1, E) [30]. Similar to DA reactions, cycloaddition reactions constructing polymer networks, leading to self-repair via four-member ring opening and closure modulated by exposure to light at different wavelengths. The recent study also reported that coumarin groups alone are able to facilitate self-healing. When coumarin pendant groups were grafted on to silicone chains, coumarin-coumarin self-associations through π-stacking result in physical crosslinking, and thermoactivated dissociation followed by re-association provide self-healing ability [31].

Dynamic exchange reactions with lower activation energies between reversible covalent bonds that proceed under mild conditions offer another opportunity for the development of self-healing polymers. Figure 1.2, A illustrates dynamics of acylhydrazone, in which acylhydrazone formation from acylhydrazine and aldehyde groups is reversible in the presence of acid catalyst [32]. Incorporation of acylhydrazone into polyethylene oxide (PEO) networks resulting in a polymer gel that self-heal at room temperature without stimuli [10]. Disulfide bonds can undergo metathesis exchange reactions in which two neighboring S-S bonds are disrupted and reformed through free radical or ionic intermediates as shown in Figure 1.2, B. [33, 34] The cleavage can be activated by photolysis, heating, or oxidation [35]. [11, 36] Mechanical properties and self-repairing abilities vary, depending upon networks morphologies. Exchange reactions
in silicone-based materials also facilitated self-repair. Figure 1.2, C depicts the siloxane exchange reactions responsible for the “livingness” promoted by the presence of tetramethylammonium dimethylsilanolate anionic end groups, which maintain their activity under ambient conditions, thus providing “ready-to-respond” active groups. A self-healing polyurea is developed by modifying urea nitrogen with bulky groups, as shown in Figure 1.2, D. The modification lowered the dissociation energy of urea C-N bond, resulting in dynamic equilibrium between urea and amine (–NH$_2$/isocyanate (–NCO) reactive groups under ambient conditions. When utilizing free-NCO groups, even physically entrapped, one needs to realize their toxicity and reactivity toward H$_2$O.

**Figure 1.2.** Exchange reactions responsible for self-healing. [Adapted from ref. [32],[11],[14, 37]]

As pointed out above, it is critical to provide sufficient time for covalent bonds to reform during network remodeling. Mechanical damage of polymers usually generates free radicals as a result of covalent bond cleavages. Recoupling of free radicals from opposite damaged surfaces will reconstruct the network by reforming covalent linkages. If the free radicals are not stabilized, oxidation processes will cause their reactivity loss, thus terminate self-healing. Dynamic reshuffling reactions involving stable free radical
formation shown in Figure 1.3 offers an interesting alternative. Taking advantage of dynamic reshuffling of trithiocarbonates (TTC) via free radical mechanism shown in Figure 1.3, A, [38] where hemolysis of C-S bonds of TTC can be photostimulated by UV radiation at 330nm generating stable free radicals which can exchange with neighboring TTC groups, self-repair property is attained. Thiuram disulfide moieties having similar reshuffling characteristics is also utilized to repair covalently cross-linked polymers.[39]

Homolytic cleavage of the disulfide is triggered by visible light, resulting in formation of dithiocarbamate-based free radicals as shown in Figure 1.3, B. It was reported that such radicals are able to remain stable for more than two weeks,[40] thus providing sufficient time for network rearrangement before recoupling. When polystyrene (PS) chains were crosslinked by dynamically reversible alkoxyamine (C-ON) groups, self-healing was achieved by thermal activated dissociation/association of alkoxyamine linkages, such as shown in Figure 1.3, C.[12] One limitation of alkoxyamines is that their stability in air. The oxidative processes may intercept re-bonding reactions. Both TTC and alkoxyamine free radicals are sensitive to air, it is therefore desirable to seek free radicals that are air tolerant. For example, cleavage of diarylbibenzofuranone (DABBF) groups create arylbenzofuranone (ABF) oxygen insensitive radicals (Figure 1.3, D), thus making poly(propylene glycol) (PPG) polymer gels crosslinked by DABBF self-repairable.[13].

When mechanical forces are evenly distributed within the network, bond rupture typically occurs at positions of lowest bond strength. For polymers, however, external forces are in fact unevenly distributed due to the presence of entanglements and crosslinked points. As a result, not only the weakest bonds, but also other covalent and non-covalent bonds may cleave depending upon the magnitude of the force.[41] While many of the self-healing studies focused only on one type of bond reformation, reactions that reconstruct multiple cleaved bonds are desirable. For example, it was identified that chain cleavages resulting from mechanical damages of crosslinked polyurethanes will generate -C•, -N• and oxygen -O• free radical intermediates. When chitosan (CHI) modified on the C6 position with four and five member heterocyclic compounds, such as oxetanes (OXE) and oxolanes(OXO), were incorporated into polyurethane (PUR) networks as shown in Figure 1.4, the low ring opening activation energy producing stable
free radicals that couple with surrounding free radicals.[9, 42] Upon mechanical damage, self-repair occurs by exposure to UV radiation. Specifically, as shown in Figure 1.4, A, four labile linkages are affected upon mechanically damage and UV radiation: -NHCONH- PUA linkage, -C-O-C- glycosine units of CHI, -C-O-C- between CHI and OXE, and –C-O-C- of OXE ring. Cleavages of these bonds generate free radicals and a carbocation. In addition, CHI pyranose ring absorb energy from UV, and undergo chair-to-boat conformation changes. Paralleled with OXE cationic ring opening catalyzed by DBTDL and PUA to PUR conversions, these processes lead to self-repair by reformation of urethane and ether linkages. Although mechanistically and kinetically different, the self-healing outcomes with oxolane-chitosan (OXO-CHI) macromonomer in PUR networks are similar. Another interesting aspect is flow of displaced polymer mass. Mechanical forces applied during damage alter the local free volume. As a result, the increase of localized free volume will favor chain mobility, thus aiding self-repairs. Thus, measurements of the local property changes on nano or micro level are desirable. As shown in Figure 6, A’, following changes of physical properties within the damages during self-repair of OXE-CHI-PUR networks using AFM tips, two T_g's are identified at 61 and 102 °C.[43] The lower T_g corresponds to PEG-polyurethane, while the higher T_g is due to OXE-CHI-urea phase. AFM measurements during repair show a repair front flow from the bottom up, followed by scratch closure upon further UV exposure.
Figure 1.4. A – Damage-repair cycle of oxetane-substituted chitosan polyurethane (OXE-CHI-PUR) network; A’ - Atomic force microscopy (AFM) images of undamaged (A’1), damaged (A’2), UV-exposed (A’2¹, A’2²) and repaired (A’3) OXE-CHI-PUR, and a plot of d(Δl)/dT vs. temperature of undamaged, damaged, and repaired networks; [9, 43]

1.2.2 Self-healing by supramolecular chemistry

Integrity of supramolecular material is achieved by the formation of non-covalent interactions.[44] This is typically accomplished by the presence of associative groups covalently attached to side chain or chain ends of the polymers, which bind the liquid-like polymers into a network with plastic or rubbery behavior resulting from non-covalent crosslinking. These interactions include hydrogen bonds, metal coordination, ionic interactions, π-π stacking, and host-guest interactions. The reversibility and speed, directionality, and sensitivity make supramolecular chemistry particularly attractive when
comes to self-healing. In contrast to covalent bonding, these networks can be remodeled rapidly and reversibly from fluid-like to solid-like states. Due to the distinct nature of secondary bonds, which differ from their polymer surroundings, the presence of associative groups usually induce morphology changes such as aggregation and crystallization.

Several successful examples of self-repairing materials using H-bonds have been developed and are shown in Table 1.2. When fatty diacids and triacids were utilized in a two-step synthetic route involving condensation of acid groups with an excess of diethylenetriamine, followed by reactions with urea, a mixture of oligomers containing H-bonding motifs including amidoethyl imidazolidone, di(amidoethyl) urea, and diamido tetraethyltriurea is obtained. Associations of the H-bonding motifs leads to the formation of the self-repairing network shown in Table 1.2, A.[17, 45] The resulting supramolecular assembly is a translucent glassy plastic which behaves like a soft rubber at temperatures up to 90 °C, and is able to self-repair at ambient conditions. The strength of directional multi-hydrogen bonds, such as triple H-bonds between thymine (Thy) and 2,6-diaminotriaine (DAT) (Table 1.2, B), [46, 47] quadruple H-bonds of ureidopyrimidinone (Upy) (Table 1.2, C), as well as multi-urea (Table 1.2, D), are comparable to covalent bonds, giving the material soft rubber like properties. Mechanical and self-healing properties are listed in Table 1, where concentration levels and the strength of supramolecular, length and rigidity of polymer backbone are the main factors determining mechanical strength and network remodeling. Flexible poly(ethylene-co-butylene) and PDMS, [49, 50] polyisobutylanes (PIB) have been used as the backbone.
polymers. Notably, H-bonding reformations often compete with external conditions, such as the presence of moisture. For example, extended moisture exposure or heating of freshly cut specimens can significantly diminish the kinetics of self-healing due to the new equilibria,[51] which has been proven for the supramolecular network shown in Table 1.2, A.

Polymers containing metal centers emerged as materials with distinct optical properties and stimuli-responsiveness. The non-covalent binding between metal and macromonomers vary from strong irreversible to highly dynamic.[52-54] The latter has essentially been utilized in self-repairing metallosupramolecular networks, offering reversibility similar to H-bonds. Their photo responsiveness offers controllable self-repairing, while reversibility and tunability by incorporating different metal ion and ligand substitutes make coordination chemistry particularly attractive. Typical metal assisted self-repairing networks are illustrated in Table 1.3.

Table 1.3 - A shows complexes formed utilizing polymers comprising of N-heterocyclic carbenes (NHCs) and transition metals.[55] When damaged, heating at 200 °C without solvent, or at 150 °C in the presence of DMSO vapor, will repair the damage due to the dynamic equilibrium between metal and the polymer, leading to flow into microcracks and reforming coordination bonds. The high repairing temperature is due to the strength of coordination bond and lack of soft segments.
Table 1.2. Reversible H-bond formations responsible for self-repair and the networks’ physical and self-repair properties: A - diacids and triacids associations from renewable resources;[17] B - triple-H-bonds formation between thymine (Thy) and 2,6-diaminotriaine (DAT);[56] C – dimerization of ureidopyrimidinone (Upy) units by quadruple-H-bonds;[49] D - copolymers combining hard polystyrene (PS) backbones with soft polyacrylate amide (PA-A) pendant groups carrying multiple H-bonding sites, and TEM image showing heterogeneity of the polymer[21].

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| **A** | Amidooethyl Imidoozolide | ![Diagram](image1.png) | • 15% soft aliphatic phase and 85% rigid phase containing H-bonds  
• Short range organization featuring 36 Å length  
• \(T_g = 8 \, ^\circ C\)  
• Tensile strength = 3.5 MPa  
• Self-repair at room temperature for 3h recovering 90% of original tensile strength |
| **B** | ![Diagram](image2.png) | ![Diagram](image3.png) | Upy-modified poly(ethylene-co-butylene)  
• \(T_g = -57 \, ^\circ C\) phase separated morphology (domain size N/A)  
• Self-repair at room temperature  
• Upy-modified poly(ethylene/propylene glycol ether)  
• \(T_g = -70 \, ^\circ C\)  
• Tensile strength = 0.35 Mpa  
• Self-repair at room temperature for 2h recover 80% of original tensile strength |
| **C** | ![Diagram](image4.png) | ![Diagram](image5.png) | **C**–dimerization of ureidopyrimidinone (Upy) units by quadruple-H-bonds;[49] D - copolymers combining hard polystyrene (PS) backbones with soft polyacrylate amide (PA-A) pendant groups carrying multiple H-bonding sites, and TEM image showing heterogeneity of the polymer[21].

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| ![Diagram](image6.png) | ![Diagram](image7.png) | ![Diagram](image8.png) | • Polystyrene core (5-40 nm) dispersed in polyacrylate amide matrix phase separated morphology.  
• Tensile strength = 3.77 MPa  
• Self-repair at room temperature for 24h recovering 90% of original extensibility |
The optically healable supramolecular polymer based on amorphous poly(ethylene-co-butylene) core with 2,6-bis(1’-methylbenzimidazolyl)pyridine (Mebip) ligands at the termini can be crosslinked via Zn (II)-bis-terpyridine coordination. This is shown in Table 1.3 - B. [18] The presence of a hydrophobic segments and the polar metal-ligand motif results in phase separated morphology. Upon exposure to ultraviolet light, the metal-ligand motifs are electronically excited and the absorbed energy is converted into heat, causing temporary disengagement of the metal-ligand motifs, and a concomitant reversible decrease in the polymers’ molecular mass and viscosity. The dissociation of the hard phase gives rise to the mobile macromonomers that will reform the original morphology, and metal-ligand coordination, facilitating healing of mechanical damages. Similar metallosupramolecular system, although chemically different compared to Zn (II)-bis-terpyridine coordination, was developed using terpyridine-Fe$^{2+}$ complexation pair with poly(alkyl methacrylate) as the main chain. This is shown in Table 1.3 – C. Elevated temperature (100 °C) can be applied to repair damages. The metal-ligand bonds remain stable at this temperature, indicating that self-repair is not caused by dissociation of the coordination bonds, but attributed to reversible formation and dissociation of 6.4 nm ionic clusters triggered by the presence of Fe$^{2+}$.

There is increasing evidence that metal-ligand coordination play an important role in the dynamics of biological rearrangements. Recent studies took advantage of coordination between Fe (III) and catechol ligands depicted in Table 1.3 - D that mimic mussel adhesives in nature, which resulted in pH-induced crosslinked self-healing polymer with near-covalent elastic moduli.[19, 57-59] The networks are formulated from
3,4 dihydroxyphenylalanine (DOPA) modified poly(ethylene glycol) (PEG) or polyallylamine. The uniqueness of this approach is the ability to switch from mono-, bis, to tris-Fe-catechol complexes at different pHs,[19] thus providing the ability of crosslinking control without Fe (III) precipitation. Similarly, crosslinked hydrogels were also prepared by complexation of branched cathehol derivatized poly(ethylene glycol) (PEG) with 1,3-benzenediboric acid. [60, 61] Later on, a heterogeneous structure inspired by mussel as shown in Table 1.3 – D was developed. [62]

Facile UV-healable polyethylenimine–copper (C$_2$H$_5$N-Cu) supramolecular polymer networks were also developed. The uniqueness of this network is that self-healing is not only induced by reversible formation of C$_2$H$_5$N-Cu complexes, but also square-planar-to-tetrahedral conformational changes of the coordination center induced by the charge transfer between σ(N) bonding and dx$^2$-y$^2$ (Cu) antibonding orbitals upon UV absorption.[63] The structural and conformational changes of the complex center are shown in Table 1.3 - E. A self-repairing polydimethylsiloxane/polyethylene glycol-polyurethane (PDMS/PEG-PUR) Cu-catalyzed networks in which Cu-O coordination was embedded into covalently crosslinked polyurethane networks were developed.[64] In addition to UV induced Cu-O bond reformation along with conformational changes, cleavage and reformation of covalent Si-O linkages were detected, indicating a multi-level repair process. Nanoindentation measurements indicated the increase of modulus inside the scratch immediately after damage. This was attributed to the formation of CuCl$_2$ clusters resulting from Cu-O bond cleavage. The interfacial property and
heterogeneity at the newly created surfaces upon damage is another area that is critical to self-repair, but has not been extensively studied.

π-π stacking interactions achieved by end-capped π-electron-deficient groups interacting with π-electron-rich aromatic backbone molecules were utilized in the development of thermal-triggered reversible self-healing supramolecular polymer networks. This was achieved by employing chain-folding copolyimide (electron deficient) and pyrenyl (electron rich) end-capped polysiloxane[65] or polyamide[66] chains. Upon heating, the π-π stacking interactions will be interrupted, enabling pyrenyl end-capped chains to disengage from copolyimide and flow due to the presence of a flexible “soft” spacer. Thus, repair of damage and regaining of mechanical strength by reformation of the π-π stacking will occur.

Table 1.3. Reversible metal-ligand coordination reactions responsible for self-repair and the networks’ physical and self-healing properties: A – dynamic equilibrium of N-heterocyclic carbenes and transition metals monomeric species and their polymer[55] B – supramolecular network containing 2,6-bis(1’-methylbenzimidazolyl) pyridine (Mebip) ligands coordinated with Zn(NTf)₂; Poly(ethylene-co-butylene) is utilized as the main chain, resulting in phase separated lamella structure as shown in the TEM image[18] C – terpyridine containing alkyl methacrylates coordinated with (iron) Fe (II) sulfate[67] D – Reversible tris catechol-Fe³⁺ complex[19] SEM images demonstrate self-assembled peptide nanofibers inter-crosslinked by catechol-Fe³⁺ complex[62] E -
polyethylenimine–copper (C₂H₅N–Cu) supramolecular polymer networks and the UV induced square planer-to-tetrahedral conformational changes[63].

Ionic interactions in polymers are primarily manifested by the formation of ionomers,[68] and selected polymers demonstrated self-healing attributes. [5] [69] [70] [71] [72, 73] [74, 75] [76] For example, in poly(ethylene-co-methacrylic acid) (EMMA) shown in Figure 10, A, polymer diffusion in a damaged area occurred under ambient and elevated temperatures upon projectile puncture testing.[5] A ballistic puncture in low density polyethylene (LDPE) did not show healing, whereas puncture in EMMA films healed the puncture leaving a scar on the surface. The proposed healing mechanism is that upon projectile impact, ionomeric network is disrupted, and heat generated by the
friction during the damage is transferred to the surroundings, generating localized melt state. The molten polymer surfaces fuse together via inter-diffusion to seal the puncture, followed by reshuffling of the ionic clustered regions and relaxation.[77]

Other reversible and potentially self-healable materials include \( \pi-\pi \) stacking interactions achieved by end-capped \( \pi \)-electron-deficient groups interacting with \( \pi \)-electron-rich aromatic backbone molecules, [78] such as those employing chain-folding copolyimide (electron deficient) and pyrenyl (electron rich) end-capped polysiloxane[65] or polyamide[66] chains. that have promising properties in bioengineering applications are based on DNA or protein crosslinks. While naturally existing host-guest assemblies exhibit great biological importance, synthetic host-guest pairs capable of reversible guest exchanges[79, 80] such as cyclodextrin’s (CD) cavity capable of entrapping other molecules, host-guest interactions between CD (host) and polyacrylic acid terminated with ferrocene (guest) also facilitate the formation of self-repairable supramolecular gels.[20, 81] Another group of reversible and potentially self-healable materials that have promising properties in bioengineering applications are based on DNA or protein crosslinks. One example are the proteins that consist of terminal leucine zipper which demonstrated reversible gel formation controlled by mild pH and/or temperature variations.[82, 83] Taking advantage of the dynamics of ‘living’ biomacromolecules and combining them with synthetic macromolecules, DNA strands were utilized to connect polymer chains to form crosslinkable networks which can be disrupted by adding unassociated DNA “fuel” strands.[84-88]
In view of the above discussion, polymer networks that rely on reversible covalent bonds and secondary interactions may offer self-repairs in which bond dynamic and chain mobility affect self-repairing efficiency. A common denominator of many studies is that rationally designed heterogeneities not only facilitate distribution of hard or soft segments and free volume, but also provide bulk integrity. Reversible bonds incorporated into hard-soft domains or their interfaces may enhance dissociation or reposition of soft domains while maintaining local integrity during repair. If designed properly, heterogeneous polymeric materials with glassy or tough rubber-like properties may offer high repair efficiency under ambient conditions. Heterogeneous materials that may also offer self-repair properties are nanocomposites. Owning to large interfacial regions, design of reversible interfacial chemistry may offer unique opportunities for development of new materials. The next sections will examine the role of interfaces in multi-phase composites and their potential impact on self-healing.

1.3 Physical Approaches for Self-Healing

Initially inspired by other disciplines,[89] introducing intentional heterogeneities into a polymer matrix resulted in the development of self-healing polymers containing hollow fibers containing reactive agents[90-93] and embedded reactive microcapsules[94, 95]. Figure 1.5 – A to C depict these processes. When hollow glass fibers shown in Figure 1.5 – A containing healing agents such as epoxies, upon mechanical damage, reactive chemicals “spilled” from damaged areas and crosslinked, thus serving as an internal glue. The alternative to hollow fibers were imbedding reactive liquid-containing microcapsules shown in Figure 10, B. Using a similar concept,
microvascular networks shown in Figure 1.5 – C offered the interconnected hollow fibers.[96-100] which enables multiple damage-cycle repairs by refilling hollow channels with healing agents upon depletion.

**Figure 1.5.** Self-healing of polymers using embedded healing agents in A – hollow fibers [adapted from refs.[90]]; B – microspheres [adapted from refs.[94]]; C – 3D microvascular networks [adapted from refs.[98]]; D – polymer matrix containing superparamagnetic nanoparticles [adapted from refs.[101]].

Critical components of this process are encapsulated reactants. Figure 1.6 – A-D illustrate chemical reactions involved in encapsulation, hollow fibers, and vascular networks. Initial micro-encapsulation experiments involved the use of catalyzed reactions of ring-opening metathesis polymerization (ROMP) of dicyclopentadiene (DCPD) microencapsulation in the presence of a ruthenium catalyst shown Figure 1.6 – A.[94, 102] Besides ROMP, siloxane, and epoxy based chemistries, isocyanate-based system also demonstrated self-healing attributes.[103] Figure 1.6 – B illustrates a two capsule system, one consisting of vinyl terminated poly(dimethyl siloxane) (vinyl-PDMS) resin and Pt catalyst complexes, and the second containing a poly(dimethyl siloxane) (PDMS)
copolymers capable of crosslinking with vinyl-PDMS via Pt catalyst.[104] Due to useful adhesive properties epoxides have been utilized as healing agents in hollow fibers[90-93] and Figure 1.6 – C illustrates epoxide/CuBr$_2$ 2-methylimidazole complex (CuBr$_2$(2-MeIM)$_4$) healing system containing microcapsules dispersed in epoxy resin.[105] 2-methylimidazole is released from the complex upon heating and initiate ring-opening polymerization of epoxide groups. Taking advantage of moisture reactive isocyanate crosslinking reactions shown in Figure 1.6 – D.

Figure 1.6. Reactions utilized in chemo-mechanical self-healing: A – ring-opening metathesis polymerization (ROMP) of dicyclopentadiene (DCPD) and ruthenium catalyst; B -- crosslinking reactions of poly(dimethyl siloxane) (PDMS) copolymer and vinyl terminated poly(dimethyl siloxane) (vinyl-PDMS) via Pt catalyst; C - epoxide/CuBr$_2$ 2-methylimidazole complex (CuBr$_2$(2-MeIM)$_4$) healing reaction; D – polymerization of isocyanate at the presence of water.
If dispersing liquid containing microcapsules, hollow fibers, or fluidic channels in a polymer matrix does not alter mechanical properties, this is perhaps a good choice for self-repairs. Numerous applications demand maintaining mechanical properties, toxicity, and release control. Although chemo-mechanical approaches require no external energy source, serving as internal glue, they exhibit various drawbacks. Nevertheless, the concept alone stimulated innovative approaches to achieve self-healing properties, perhaps the most appealing extension of encapsulation is remote self-healing.

It is well known that polymers in a molten state will exhibit significantly enhanced chain mobility and interfacial diffusion. If interfacial diffusion is induced locally in a damage area of a polymer, it will facilitate repairs. This is achieved by incorporating superparamagnetic $\gamma$-Fe$_2$O$_3$ nanoparticles into a thermoplastic polymer network as depicted in Figure 1.5 – D.[101] The $\gamma$-Fe$_2$O$_3$ nanoparticles oscillate at the frequency by applying oscillating magnetic field, thus increase the nanoparticle-polymer interface temperature. Generated localized melt flow permanently repair physically separated polymer interfaces and the process can be repeated multiple times. Using a similar concept, the use of selective wavelengths to initiate self-healing that converts electromagnetic radiation to other form of energy is another unique approach, such as dispersing graphene layers in a polyurethane matrix to absorb microwave energy and convert it into heat.[106] Another example is embedding silver nanoparticles that exhibit surface plasma adsorption bands in the visible range of electromagnetic radiation inside the capsules[107] which offered the advantage of photo-induced heating enhanced by plasma resonances from the metal nanoparticles. The use of noble metal nanoparticles
offers new opportunities for the use of tunable energy sources capable of high efficiency localized conversions of electromagnetic radiation to heat.[108, 109] Taking this concept further, nonlinear optical materials with plasmonic properties were developed. For example, gold colloids containing zinc phthalocyanines[110] that exhibit self-repairing photo-fragmented nanoparticles offered the advantage of remotely triggered responses.[111]

Intuitively, rigid nanoparticles, nanotubes, or fibers within composite materials will not contribute to self-repair, unless they have inherently built-in self-healing components. However, if interfacial regions between polymer matrix and reinforcing rigid entities exhibit the ability of bond cleavage and reformation, interfacial regions may serve that purpose. The majority of nanoparticles, nanorods/nanowires, nanotubes, nanofibers, and graphene sheets can be surface modified to generate amine,[112] carboxylic acid,[113] hydroxyl,[114] UPy,[115] thiol,[116] furfuryl,[117] cinnamoyl,[118] anthracene,[119] or pyrenyl groups[120], which can react with their counterparts in the matrix. Thus, the nature of modifications will be determined by the polymer motif to form reversible bonds with a polymer matrix. Consequently, interfacial chemistry will be critical in achieving reversible self-repair. Figure 1.7 summerizes commonly utilized nanomaterials (A) and their surface functionalizations (B). For surface functionalization to be effective, polymer matrix should consist of “matching” reactive groups, which are illustrated in column C. Thus, when B and C react, interfacial bonding in column D will facilitates covalent and non-covalent interfacial interactions. One can envision that reforming bonding at the fiber-matrix interface may facilitate repairs when
the interface undergoes partial damage-repair cycle, but overall mechanical integrity of a composite is retained. When a load is removed, the reformed interface will return to equilibrium conditions. This is schematically illustrated in Figure 1.7 – E.

**Figure 1.7** A - Nanomaterials; B. Selected surface modifications for nanomaterials; C - Polymer matrix functional groups; D - Covalent/dynamic bonding formation between
nanomaterials and a polymer matrix; E – Schematic illustration of dynamic interfacial rebonding in nanocomposites; driven by the partial dissociation of interfacial bonding under shear forces, followed by reforming cleaved interactions.
CHAPTER 2  SELF-HEALING POLYURETHANE NETWORKS BY
ATMOSPHERIC CARBON DIOXIDE AND WATER

2.1 Introduction

Numerous studies have shown that reversible breaking and reforming of dynamic covalent[8-15] or non-covalent[5, 16-21] bonds can lead to self-healing. However, the use of environmental gases in materials’ self-repair has never been explored. It is well established though that plants assimilate carbon dioxide (CO\textsubscript{2}) and water (H\textsubscript{2}O) to produce organic compounds releasing oxygen (O\textsubscript{2}).[121] As a result, carbohydrates are produced, and the carbon fixation cycle is one of the essential steps in this process. Can man-made materials utilize atmospheric gases to renew themselves? Notably, the use of CO\textsubscript{2} as a raw material to produce organic compounds has been explored, and many successful reactions of CO\textsubscript{2} with methanol, diols, and cyclic ethers to produce dimethyl carbonates, cyclic carbonates, and polycarbonates have been reported.[122-124] Furthermore, under certain catalytic conditions, CO\textsubscript{2} also reacts with primary or secondary amines to form urethanes and ureas.[125] Interestingly enough, when polyurethanes (PUR) are synthesized in the presence of H\textsubscript{2}O vapors, CO\textsubscript{2} as well as polyurea (PUA) can be generated. The PUR networks shown in Figure 2.1, A are produced by reacting polyethylene glycol (PEG) and hexamethylene diisocyanate trimer (HDI), resulting in PUR and PUA segments as well as gaseous CO\textsubscript{2}. If such PUR network is mechanically damaged, during which C-O, C-N, and other linkages are cleaved, CO\textsubscript{2} and H\textsubscript{2}O will not facilitate self-repair. However, if carbohydrates with multiple hydroxyl (OH) groups are incorporated into PURs, will CO\textsubscript{2} and H\textsubscript{2}O be able to
regenerate mechanically damaged network bonds? To test this hypothesis we incorporated monosaccharides, such as methyl-α-D-glucopyranoside (MGP) containing four reactive OH groups, into crosslinking reactions of HDI and PEG. These reactions were catalyzed by dibutyltin dilaurate (DBTDL) to form MGP modified polyurethane (MGP-PUR-DBTDL) networks. Such networks were subjected to controllable mechanical damage.

2.2 Experimental Methods

Methyl α-D-glucopyranoside (MGP), polyethylene glycol (PEG), hexamethylene diisocyanate (HDI monomer), N,N-Dimethylformamide (DMF), dibutyltin dilaurate (DBTL), copper(II) chloride (CuCl₂), magnesium chloride (MgCl₂) hexahydrate were purchased from Sigma Aldrich Co., tri-functional hexamethylene diisocyanate polymer (HDI trimer) N3300a was purchased from Bayer. Carbon dioxide (CO₂) and oxygen (O₂) gases were purchased from Airgas National.

MGP-PUR-DBTDL films were prepared by reacting HDI trimer with MGP and PEG in DMF using overhead agitation at 500 rpm with a small four-blade polytetrafluoroethylene (PTFE) impeller in a 50 ml three-neck reaction flask at 25 °C for 10 min. MGP-PUR networks were formed by reacting HDI trimer, PEG and MGP using stoichiometric amounts of NCO and OH groups. The molar ratio of HDI trimer/PEG/MGP = 1/0.69/0.81 were utilized while maintaining 38% (w/w) solids. This ratio was utilized to react two out of four OH groups of MGP with NCO. Such mixtures were applied to obtain an approximate film thickness of 300 µm (± 4 µm) on a PTFE substrate at 75 °C and dried for 48 hours.
Specimen damages were achieved by creating scratches with precisely controlled dimensions using custom built computerized Micro-Cut Instrument that facilitates control of the depth, speed and load during damage. In a typical experiment, a speed of 5 mm/s and a depth of 100 μm were utilized to obtain a 20 μm width and 100 μm deep scratches.

Optical images were recorded using Leica DM2500 M microscope. 3D optical images were generated by analyzing the shades of optical images using ENVI software (The Environment for Visualizing Images, Research Systems, Inc.) version 3.5.

Relative humidity (RH) was controlled by utilizing enclosures containing saturated magnesium chloride solutions (RH=28 ± 2 %) and monitoring RH by humidity meter (Fisher Scientific Traceable Hygrometer).

Internal reflection infrared images (IRIRI) were obtained using a Cary 600 series Stingray system equipped with internal reflection IR imaging providing 1 micron spatial resolution. This system consists of a Cary 680 spectrometer, a Cary 620 FTIR Microscope, an image IR focal plane array (FPA) image detector, and germanium (Ge) imaging crystal. The IR images were collected using the following spectral acquisition parameters: under sampling ratio 2, rapid-scan speed 5Hz, number of images per step 64, and spectral resolution 4 cm$^{-1}$. Image processing was performed using ENVI software (The Environment for Visualizing Images, Research Systems, Inc.) version 3.5. Traces showing IR spectra inside and outside damage were averaged over 20 spectra.
Microscopic attenuated total reflectance Fourier transform infrared spectra (µATR FT-IR) were obtained using an Agilent Cary 680 FT-IR single-beam spectrometer setting at 4 cm\(^{-1}\) resolution. A 2 mm diamond crystal, and maintain constant contact pressure between crystal and the film specimens was used. All spectra were corrected for spectral distortions and optical effects using Urban-Huang algorithm.[126]

Raman spectra were recorded using a Renishaw inVia Raman microscope equipped with a computer controlled three-axis encoded (X, Y, Z) motorized stage, a RenCam CCD detector, and a Leica microscope (DM2500 M). The 785 nm diode laser at 100mW power provided an excitation source. The films were placed on the gold surface and an acquisition time of 60 sec was used.

Molecular structure of equilibrated center of chelation complexes was obtained using Avogadro software. The geometry optimization was produced under UFF force field.

Dynamic mechanical analysis (DMA) were performed on a TA Instrument Q800 DMA. Rectangular specimens having a size of 15.73 mm×6.09 mm×1.07 mm were tested at a frequency of 10 Hz. Dynamic mechanical properties were measured from -100°C up to 80°C while heating at 2°C/min. Dynamic moduli and mechanical damping (tan δ) were analyzed using TA Universal Analysis 2000. The measured glass transition temperature (\(T_g\)) for MGP-PUR at maximum tan δ is 54 ± 1°C.
Nano-indentation measurements were performed on Ti 950 TriboIndenter equipped with a diamond Berkovich probe. Storage modulus was measured at 220 Hz frequency, 4 μN dynamic load, and a peak force of 1000 μN. Tensile stretch test was carried out on Instron 4502 at room temperature (25 °C) at a rate of 2 mm/min. Repaired MGP-PUR-DBTDL for tensile stretch test was prepared by cutting and physically separating the film, followed by attaching the separated parts together. After self-repair under ambient conditions for 30 min, the film was subject to tensile test.

Energy-dispersive X-ray (EDX) spectroscopy was collected on Hitachi Variable Pressure Scanning Electron Microscope (SEM) SU6600 equipped with EDX system at a working distance of 10mm, an accelerating voltage of 20 kV, and variable pressure mode (30 Pa). Weight % atoms of carbon (C), oxygen (O), nitrogen (N), and tin (Sn) inside and outside the scar were measured using points collection mode, and each averaged over 5 points.

2.3 Results and Discussion

2.3.1 Self-healing Properties of MGP-PUR-DBTDL

Figure 2.1, B illustrates the reactions leading to MGP-PUR-DBTDL formation. Glass transition temperature ($T_g$) of the resulting polymer is 56 °C measured by dynamic mechanical analysis (Figure A-1 of Appendix A). Upon damage-repair cycles under controlled conditions as described in the Experimental session, Figure 2.1, C illustrates that, indeed, such networks are capable of self-repair in air under ambient conditions. In contrast, when the same damaged MGP-PUR-DBTDL network is exposed to pure $N_2$, $O_2$, $CO_2$, or $H_2O$ (28 % RH in $N_2$), no self-repair occurs. The results of these experiments are
illustrated in Figure 2.2. However, exposure to pure CO$_2$ at 28% RH facilitates MGP-PUR network repair. This is shown in Figure 2.1, D. For comparison, PUR networks without crosslinked MGP shown in Figure 2.1, E do not exhibit these unique attributes. These experimental results clearly demonstrate that the covalent incorporation of MGP into PUR networks catalyzed by DBTDL, such as shown in Figure 2.1, B, facilitates self-repair under CO$_2$ and H$_2$O atmosphere. The question is what molecular processes may govern this unique behavior, and what molecular entities are formed as a result of autonomous repair?
**Figure 2.1.** A – Reactions of isocyanate (NCO) groups of HDI and hydroxyl (OH) of PEG in the presence of H₂O generate CO₂ during PUR formation; B – Reactions of NCO groups of HDI and OH of PEG and MPG in the presence of H₂O result in MGP-PUR-DBTDL network formation. Each network linkage and/or component is identified as follows: PUA - polyurea; HDI – hexamethylene diisocyanate trimmer; PUR – polyurethane; PEG – polyethylene glycol; MGP – methyl-α-D-glucopyranoside. Self-repair of MGP-PUR-DBTDL network exposed to: C – air at 25 °C; D – Self-repair of MGP-PUR-DBTDL network exposed to the CO₂/H₂O mixture; E – Self-repair is not observed for PUR-DBTDL itself exposed to air.

**Figure 2.2.** Optical images of damaged MGP-PUR-DBTDL networks exposed to: A – N₂; B – O₂; C – CO₂; D – H₂O vapor (28% RH in N₂); E – MGP-PUR-DBTDL network catalyzed by CuCl₂ and exposed to air (the same condition as in Figure 2.1, C).
2.3.2 Spectroscopic analysis of the self-healing mechanism

To identify molecular events responsible for self-repair of MGP-PUR-DBTDL we followed chemical changes during damage-repair cycle using internal reflection IR imaging (IRIRI). This analytical tool, complimented by Raman spectroscopy, allows us to determine chemical changes inside scratch during damage-repair cycle with a spatial resolution of ~1 μm². [127] Figure 2.3, A and B illustrate optical images recorded 1 (A) and 30 mins (B) after damage. Figure 2.3, A-1 – A-5 and B-1 – B-5 show the corresponding IRIRI images collected from 30×30 μm² area of the 1680 (A-1 and B-1), 1558 (A-2 and B-2), 1427 (A-3 and B-3), 1376 (A-4 and B-4), and 1045 (A-5 and B-5) cm⁻¹ bands that are most sensitive to damage-repair cycle. While x-y directions identify spatial distribution of these bands, their intensity changes (z-direction) are also reflected in color variations (red-high; blue-low). The corresponding spectra recorded inside scratch (a/a’) and outside (b/b’) damaged area are shown in Figure 2.3, A’-1 – A’-5 and B’-1 – B’-5. As manifested by the band intensity and color changes of IRIRI images collected 1 min after damage (Figure 2.3, A-1 - A-5), and the corresponding IR spectra in Traces A’-1 - A’-5 in Figure 2.3, multiple bond cleavage occur upon mechanical damage. Relevant IR vibrational bands detected in MGP-PUR-DBTDL networks and their assignments are listed in Table A-1 of Appendix A.

The 1680 cm⁻¹ band due to H-bonded urethane C=O stretching vibrations decreases, while the 1715 cm⁻¹ band due to the non-H-bonded urethanes increases (Figure 2.3, A-1 and A’-1), indicating cleaved of PUR bond and dissociation of H-bonding. Furthermore, the increase of the 1620 cm⁻¹ band due to N-H deformation of primary amines (NH₂)
(Figure 2.3, A’-1) resulting from breakage of urethane C-N and C-O bonds and subsequent hydrogen abstraction is observed. The C-O bond dissociation in PEG segments is manifested by the decrease of the 1350 cm\(^{-1}\) band (C-H deformation of ether linkages) (Figure 2.3, A’-4). H-bonding dissociation is further substantiated by the decrease of the N-H and O-H stretching vibrations at 3346 cm\(^{-1}\) (Figure 2.4), which overshadows spectroscopic changes due to hydrolysis of ether segments. Also, the bands at 1558 (Figure 2.3, A-2 and A’-2), 1427 (Figure 2.3, A-3 and A’-3), and 1376 (Figure 2.3, A-4 and A’-4) cm\(^{-1}\) exhibit slight intensity increase 1 min after damage, which significantly increase during self-repair process. The increases of the 1142, 1100, and 1045 cm\(^{-1}\) bands (Figure 2.3, A-5 and A’-5) attributed to C-O stretching vibrations result primarily from conformational changes of HCO groups of MGP, C-O-C groups of PEG, and/or PEG/PUR C-O-C linkages. In summary, C-N and C-O covalent bond cleavage as well as urethane H-bonding dissociation are the main observed molecular events dominating mechanical damage.
Figure 2.3. A - Optical image of MGP-PUR-DBTDL film 1 min after damage; B - optical image of MGP-PUR film self-repaired 30 min after damage. Analyzing the shades on the original 2-D optical images using Envi program generated the 3-D depth profiles of the optical images. Images A1 through A5 represent 3D intensity distributions of vibrational bands at 1680 (A-1), 1558 (A-2), 1427 (A-3), 1376 (A-4), and 1045 cm\(^{-1}\) (A-5) recorded from a square marked on Figure 2.3, A. Traces A’-1 through A’-5 represent IR spectra collected from areas a and b of images A-1 through A-5 respectively (a - spectra collected inside scratch 1 min after damage; b - spectra collected from...
undamaged area). Images B1 through B5 represent 3D intensity changes of vibrational bands at 1680 (B-1), 1558 (B-2), 1427 (B-3), 1376 (B-4), and 1045 cm\(^{-1}\) (B-5) recorded from a square marked on Figure 2, B. Trances B’-1 through B’-5 represent IR spectra collected from areas a’ and b’ of images B-1 through B-5 (a’ - spectra collected from damaged area after repair; b’ - spectra collected from undamaged area).

Figure 2.3, B illustrates the results of spectroscopic analysis after repair under atmospheric CO\(_2\) and H\(_2\)O (28% RH and 25°C). The intensity decreases of the urethane C=O stretching bands at 1715 and 1680 cm\(^{-1}\) (Figure 2.3, B-1 and B’-1) are detected, whereas the band at 1558 cm\(^{-1}\) (Figure 2.3, B-2 and B’-2) increases. This is attributed to Sn-chelation with C=O entities [128] of MGP during repair of MGP-PUR-DBTDL networks. Even though only 10\(^{-5}\) mol/g concentration levels of DBTDL were used to catalyze MGP-PUR network formation, significant increase of the bands due to DBTDL vibrations at 1558 cm\(^{-1}\) (Sn····O=C), 1376 cm\(^{-1}\) (C-H bending) (Figure 2.3, B-4 and B’-4), 2856 and 2923 cm\(^{-1}\) (C-H stretching) (Figure 2.4) are detected in repaired areas. These observations are attributed to chelation and conformational changes of DBTDL during repair. We utilized energy-dispersive X-ray spectroscopy (EDX) to measure Sn concentrations inside and outside scratch. Figure 2.5 shows that indeed Sn content remains unchanged. However, the concentration levels of carbon increase in the repaired area. In summary, the above data show that, in addition to CO\(_2\) and H\(_2\)O atmosphere, MGP and DBTDL play a significant role during self-repair process. When copper(II) chloride (CuCl\(_2\)) was utilized as a catalyst in the same MGP-PUR-DBTDL networks, no self-repair was observed (Figure 2.2, E). It should be noted that CuCl\(_2\) is capable of
catalyzing and facilitating repairs of polydimethylsiloxane-polyurethane (PDMS-PUR) crosslinked networks.[129] Thus, only specific reactions catalyzed by DBTDL will facilitate PUR self-repair.

![Figure 2.4. ATR-FTIR spectra of damaged and repaired MGP-PUR-DBTDL networks obtained from IRIRI images (Figure 2.3). The spectra were collected from marked square areas in Figure 2.3, A-1 through A-5 and B-1 through B-5; a - inside a scratch 1 min after damage; b – undamaged area 1 min after damage; a’ – damaged area after repair; b’ – undamaged area after repair.](image)

To verify spectroscopic changes under atmospheric CO$_2$ and H$_2$O, we conducted a series of controlled experiments. Control molecules were synthesized with various concentrations of MGP, HDI monomer and DBTDL, and interactions of individual molecule in the context of self-repair of MGP-PUR-DBTDL were examined. MGP and HDI monomers were reacted following the same procedure as for MGP-PUR-DBTDL networks by varying MGP:HDI monomer ratios: MGP:HDI =1:0.5 (a), 1:1(b) , 1:1.5 (c) and 1:2 (d). These ratios correspond to 1, 2, 3, and 4 OH groups of MGP reacted with
NCO groups. For each ratio, three concentrations of DBTDL, $0.2 \times 10^{-5}$, $1 \times 10^{-5}$, $20 \times 10^{-5}$ mol/g, were used. All specimens were analyzed using ATR FT-IR. Figure 2.6 provides further details of ATR FT-IR analysis and showed that the degree of Sn⋯O=C chelation is the strongest when, on average, two OH groups of MGP are reacted with NCO. If MGP is not utilized at all, instead of Sn⋯O=C chelation manifested by significant increase of the 1558 cm\(^{-1}\), this band shifts to 1565 cm\(^{-1}\) (Figure 2.7). These results are further substantiated by the decrease of the 1335 cm\(^{-1}\) band due to CCH deformations of the MGP ring resulting from conformational changes of the ring substituents upon chelation.[130] This is shown in Figure 2.3, B-4 and B’-4 as well as Figure 2.6.

Considering that OH groups in C2 and C6 positions of MGP exhibit highest reactivity compared to C3 and C4, (Figure 2.1, A) whereby C6 is greater than C2,[131] when only C6 OH react with NCO, no chelation is observed. However, when OH in C2 position is reacted, chelation with DBTDL is the strongest.

<table>
<thead>
<tr>
<th></th>
<th>1 min after damage</th>
<th>30 min after damage</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Weight % of atoms</td>
<td>C</td>
</tr>
<tr>
<td>Inside scratch</td>
<td>24.74±0.19</td>
<td>72.82±0.01</td>
</tr>
<tr>
<td>Outside scratch</td>
<td>25.63±0.12</td>
<td>72.78±0.01</td>
</tr>
<tr>
<td>Inside scratch</td>
<td>25.88±0.26</td>
<td>72.77±0.01</td>
</tr>
<tr>
<td>Outside scratch</td>
<td>25.48±0.19</td>
<td>72.78±0.02</td>
</tr>
</tbody>
</table>

**Figure 2.5.** SEM images of mechanically damaged MGP-PUR-DBTDL film: A – 1 min after damage; B – 30 min after damage. Corresponding concentration levels of C, O, N,
and Sn (w/w %) inside and outside damage/repaired area measured using XRD: Table A’ - 1 min after damage; Table B’ - 30 min after damage. The data were averaged over five measurements.

As identified in Figure 2.3, A, dissociation of covalent bonds occurs during mechanical damage. The question is whether these bonds reform, and what structural entities result from repair. IRIRI analysis collected on a repaired scar revealed the increase of the urethane C-N stretching band intensities at 1247 cm$^{-1}$ along with the decrease of N-H stretching at 3346 cm$^{-1}$ (Figure 2.4). These changes are caused by reformation of urethane linkages. In the C-O region, the 1142 cm$^{-1}$ band due to OCH bending of MGP decreases, and the 1045 cm$^{-1}$ band due to C-O stretching vibrations continues to increase (Figure 2.3, B-5 and B’-5).[130] These changes result from substitution of MGP-OH with urethane groups. The same changes are detected for 1142 and 1045 cm$^{-1}$ bands in the control experiments in which hydroxyl on MGP was reacted with NCO (Figure 2.6). The increase of the C-H bending vibrations at 1427 cm$^{-1}$ (Figure 2.3, B-3 and B’-3) due to asymmetric C-H deformation next to tertiary amides further substantiate these network rearrangements. Thus, reformation of C-O and C-N bonds occur as a result of substitution of the C3 and C4 OH groups of MGP. Furthermore, two new bands at 1750 (Figure 2.3, B’-1) and 1127 cm$^{-1}$ (Figure 2.3, B’-5) due C=O and C-O-C stretching, which were not observed before, are detected (Figure 2.3, B’-1 and B’-5). Their presence is attributed to carbonate linkage formations. [132]
It should be noted that these spectroscopic changes are only detected in the presence of CO$_2$ and H$_2$O. IRIRI images collected from MGP-PUR-DBTDL specimens in damaged and undamaged areas after 30 min exposure to N$_2$, H$_2$O, and CO$_2$ are shown in Figure 2.8. No intensity changes due to bond reformation are detected. When damaged MGP-PUR-DBTDL network is exposed to CO$_2$, the band at 1565 cm$^{-1}$ due to C=O stretching of DBTDL increases. The formation of Sn and MGP-urethane complex or substitution of MGP-OH is not observed under these conditions. These data indicate that CO$_2$ gas molecules interact with DBTDL in damaged areas, but in order to reform covalent linkages, the presence of H$_2$O and CO$_2$ is required.
Figure 2.6. A - ATR FT-IR spectra of MGP-HDI specimens prepared with the following MGP:HDI monomer ratios: 1:0.5 (Traces a (−)), 1:1(Trace b (−)), 1: 1.5 (Trace c (−)), and 1:2(Trace d (−)). B - ATR FT-IR spectra of MGP-HDI specimens prepared using the same MGP:HDI monomer ratios as in Figure 2.6, A with varied DBTDL concentration levels. Spectra a′/a″, b′/b″, c′/c″, and d′/d″ correspond to 1:0.5 (Traces a), 1:1(Trace b), 1: 1.5 (Trace c), and 1:2 (Trace d) ratios of Figure 2.6, A. For each ratio, three concentrations of DBTDL, $0.2 \times 10^{-5}$ (−), $1 \times 10^{-5}$ (−), and $20 \times 10^{-5}$ (−) mol/g, were used.
It should be noted that during a single internal reflection experiment using Ge crystal such as in IRIRI experiments, when bonds are ruptured by mechanical forces, the Ge probe is in contact with the surface. At 45° angle of incidence, the signal carrying chemical information comes from approximately ~650 nm depth.[133] Assuming that the top 10 nm of surface contain 100% of cleaved bonds, the overall detected signal will consist of roughly 98.5% of uncleaved (~650 nm depth) and 1.5% of cleaved bonds (~10 nm). Therefore, anticipated intensity changes are in the range of 1.5% of the overall band intensities. In an effort to confirm that relatively small changes are attributed to damage-repair cycle, control experiments utilized larger quantities of reactants. Thus, they provide confirmation and evidence that even small intensity changes in multiple IRIRI experiments are due to damage-repair cycle.

![Figure 2.7](image)

**Figure 2.7.** FT-IR spectra of PUR-DBTDL obtained using IRIRI collected from damaged and undamaged areas 30 min after mechanical damage.
In an effort to confirm IR analysis results, Raman spectroscopy was utilized to determine bond reformations 30 min after damage. As shown in Figure 2.9, the most sensitive bands at 1412, 866, and 661 cm\(^{-1}\) are due to urethane and carbonate vibrations. These bands increase as a result of bond reformation and repair.

Figure 2.8. IRIR images of damaged MGP-PUR-DBTDL networks obtained by tuning into the 1680 cm\(^{-1}\) band after 30 min exposure to: A – N\(_2\); B – H\(_2\)O; and C – CO\(_2\). FT-IR spectra A’, B’ and C’ represent traces collected from the areas a, a’, a” (inside scratch) and b, b’, b” (undamaged area) marked in the images A through C, respectively.
In summary, formations of urethane and carbonate functional linkages are primarily responsible for self-repair of MGP-PUR-DBTDL networks. Thus, the primary event is the Sn chelation with MGP-urethane, and covalent substitution of MGP-OH moieties leading to the formation of urethane and carbonate linkages.

2.3.3 Mechanical analysis of the self-healing effect

Mechanical properties of undamaged and repaired MGP-PUR-DBTDL specimens were also analyzed. MGP-PUR-DBTDL films were cut into two pieces. Self-repair was conducted by re-attaching two separated pieces under ambient conditions, followed by stress-strain measurements. Figure 2.10 summarizes the results, which show that incorporation of MGP to form MGP-PUR-DBTDL networks results in the increase of the

**Figure 2.9.** Raman spectra of MGP-PUR-DBTDL collected from: Trace a – damaged areas after 30mins; Trace b - undamaged areas.
Young's modulus (E) from 3.58 for PUR to 77.7 MPa in MGP-PUR-DBTDL. The maximum stress of undamaged MGP-PUR-DBTDL is 12.97 MPa at the maximum elongation of 227%. Upon self-repair, the maximum stress diminishes to 3.38 MPa at 48% elongation. In another experiment, we created a scratch on a MGP-PUR-DBTDL film and measured storage modulus E’ inside the scratch (nano-indentation) at the oscillation depth of 200 nm. During ~30 min of self-repair, the E’ values inside the scratch increase from ~1.9 to ~4.5 GPa. Table 2.1 summarizes these results. Notably, there in an initial drop of the E’ values from 1.9 to 1.1 GPa, followed by the expected increase to reach ~4.5 GPa. For the undamaged MGP-PUR, the E’ values are ~2.8 GPa. The initial drop of the E’ values (during the first 10 min) is likely attributed to the adsorption of CO\textsubscript{2} and H\textsubscript{2}O capable of plasticizing damaged network, thus enhancing segmental mobility of cleaved segments. Comparison of the stress-strain and storage moduli measurements shows different rates of the recovery. The storage moduli were measured inside scratch, whereas the stress-strain curves were obtained from bulk measurements. Under stress-strain experimental conditions, CO\textsubscript{2} and H\textsubscript{2}O diffusion to the inside part of damage is limited, thus not all bonds can be reformed during the timeframe of these experiments. This is reflected in lower maximum stress/elongation at break after repair. In contrast, when scratch is created and nano-indentation experiments are performed, CO\textsubscript{2} and H\textsubscript{2}O may easily diffuse into damaged areas, thus reaching full recovery of the E’ values.
Figure 2.10. A – Stress-strain curves of: a - undamaged MGP-PUR-DBTDL, b - repaired MGP-PUR, and c - neat PUR. Young’s moduli, elongation at break, and stress at maximum load are summarized in part B. Optical images C illustrate: C-1 – undamaged MGP-PUR film; C-2 – cut and physically separated MGP-PUR film; C-3 – physically attached previously separated parts; and C-4 – self-repair film after 30 mins.

Storage (E’), loss (E”) moduli, and tan δ were measured using dynamic mechanical analysis (DMA). DMA results for PUR-DBTDL (A) and MGP-PUR-DBTDL
are shown in the Figure A-1 of Appendix A. The glass transition temperature (T\textsubscript{g}) of PUR increases from 2°C to 54°C by covalent incorporation (crosslinking) of MGP into PUR networks (Figure 2.1, B). Table 2.1 summarizes storage moduli recorded inside and outside scratch during 30 min of self-repair process using nano-indentation.

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>0</th>
<th>10</th>
<th>20</th>
<th>30</th>
</tr>
</thead>
<tbody>
<tr>
<td>Storage modulus (E’) inside scratch (GPa)</td>
<td>1.9 ± 0.1</td>
<td>1.1 ± 0.05</td>
<td>2.9 ± 0.3</td>
<td>4.5 ± 0.5</td>
</tr>
<tr>
<td>Storage modulus (E’) outside scratch (GPa)</td>
<td>2.3 ± 0.1</td>
<td>2.2 ± 0.1</td>
<td>2.8 ± 0.2</td>
<td>2.8 ± 0.3</td>
</tr>
</tbody>
</table>

**Table 2.1.** Storage modulus (E’) of MGP-PUR-DBTDL inside newly created scratch and outside of the scratch measured as a function of time at the oscillation depth of ~200 nm.

2.3.4 Proposed self-healing mechanism

Supported by spectroscopic evidence discussed in Figure 2.3, the mechanism of MGP-PUR-DBTDL self-repair under atmospheric conditions is depicted in Figure 2.11. Figure 2.11, A depicts that two main molecular events due to mechanical damage are free radical generation and H abstraction. The proposed mechanism for self-repair is shown in Figure 2.11, B. Facilitated by initial coordination with H\textsubscript{2}O, Sn complexes with MGP through chelation with the neighboring MGP-OH and urethane C=O groups to form a ring structure (a). This intermediate was spectroscopically identified as Sn····O=C chelated ring and molecular modeling shown in Figure 2.11, C identified that this complex during self-repair is energetically most favorable conformation. The next step
involves CO$_2$ insertion into Sn-O bonds to form carbonate moieties (Figure 2.11, B(b)). It should be noted that the majority of CO$_2$ insertion reactions to Sn-O bonds are conducted under 1 atm of CO$_2$. [134-136] Reactions shown in Figure 2.11 occur upon MGP-urethane and Sn complexation facilitates CO$_2$ insertion (b) and subsequent carbonate (c) and urethane (d and e) formation. During this step, metal carbonate moieties shown in Figure 2.11, B(b) are subject to nucleophilic attack. As shown spectroscopically, three main nucleophilic sites are present after damage: PEG-OH after cleavage of PEG C-O-C bonds, N-H moieties of urethanes, and NH$_2$ resulting from cleavage of urethane linkages. Reactions with PEG-OH nucleophiles result in formation of carbonate linkages (Figure 2.11, B(c)), and N-H and NH$_2$ groups result in the reformation of urethane linkages (Figure 2.11, B(d) and (e) respectively). Although kinetics of each of these reactions remains to be determined, these reactions facilitated self-repair of MGP-PUR-DBTDL networks.
Figure 2.11 A – Bond cleavages due to mechanical damage; B - Mechanism of leading to the formation of carbonate and biurethane linkages; C - Optimized molecular structure of MGP-urethane, Sn, and CO$_2$ complex.

2.4 Conclusions

We developed crosslinked polyurethane networks containing crosslinked sugar moieties capable of self-repair under atmospheric conditions at ambient temperatures
without intervention. By incorporating sugar moieties into polyurethanes, these materials are able to react with atmospheric CO$_2$ and H$_2$O, thus reforming covalent linkages capable of bridging cleaved network segments. Mechanical properties are recovered during self-repair process. These materials resemble behavior of plants during photosynthesis, which convert CO$_2$ and H$_2$O into carbohydrates.
CHAPTER 3 SELF-HEALING OF POLYMER NETWORKS BY DAMAGE-INDUCED PRIMARY AMINES; METABOLIC REACTIONS IN SYNTHETIC MATERIALS

3.1 Introduction

While the majority of synthetic approaches utilized one or two types of re-bonding mechanisms imbedded into a known polymer matrix to facilitate self-healing, in contrast, even for the most primitive biological species, chemical and physical events responsible for repairs and their living functions exhibit significantly greater degree of complexity. In metabolic processes molecules used for reconstructing cell components are produced from the breakdown of organic matter, which facilitate the maintenance of living functions. Perhaps one of most representative reactive functional groups are amines, which are responsible for such processes as protein binding, cellular recognition, enzyme and peptide functions, and many others. Synthetic materials may be capable of responsiveness in the form of adaptiveness, self-repair, and reproductive abilities, if they are programed to activate reactive groups upon external stimuli.

Realizing that the strength of covalent re-bonding of amines utilized in biological systems leads to regaining of a structural integrity of living organisms, our recent efforts focused on the design of synthetic networks capable of generating primary amines. This section reports the development of methyl α-D-glucopyranoside (MGP)-modified polyurethane networks catalyzed by zinc acetate (Zn(OAc)₂) (MGP-PUR-Zn(OAc)₂) that are capable of generating reactive groups upon mechanical damage. Since there is an increasing evidence that dynamic reformations of bonds can be facilitated by a
combination of physical and chemical events,[137] the choice of components was dictated by the premise that the formation of reactive groups upon mechanical damage will lead to covalent re-bonding. The synthesis of the crosslinked network is illustrated in Figure 3.1, A, where MGP, and polyethylene glycol (PEG, Mₚ=300 g/mol) were reacted with hexamethylene diisocyanate crosslinker (HDI) in the presence of Zn(OAc)₂.

3.2 Experimental Methods

Methyl α-D-glucopyranoside (MGP), polyethylene glycol (PEG, Avg Mn = 300 g/mol), hexamethylene isocyanate (HI), anhydrous N,N-Dimethylformamide (DMF), tetrahydrofuran (THF), zinc acetate (Zn(OAc)₂), 2,2′-(Ethylenedioxy)bis(ethylamine) (EDBEA), butanediol, were purchased from Sigma Aldrich Co., tri-functional hexamethylene diisocyanate polymer (HDI trimer) N3300a was provided by Covestro.

MGP-PUR-Zn(OAc)₂ films were prepared by reacting HDI trimer with MGP in DMF in the presence of Zn(OAc)₂ catalyst using overhead agitation at 500 rpm with a small four-blade polytetrafluoroethylene (PTFE) impeller in a 50 ml three-neck reaction flask at 25 °C for 10 min. Then PEG was added and continued to react for another 5 min. The molar ratio of HDI trimer/PEG/MGP = 1/0.69/0.41 were utilized while maintaining 38% (w/w) solids. Such mixtures were applied to obtain an approximate film thickness of 1 mm (± 0.1 mm) on a PTFE substrate and dried at 75 °C for 5 days. The resulting MGP-PUR-Zn(OAc)₂ films with 1.2% w/w Zn(OAc)₂ exhibit a glass transition temperature (Tₐ) of 56 °C measured by DMA, Young’s modulus of 77.8 MPa at 20 °C measured by tensile analysis, and the molecular weight between crosslinks (Mₓ) of 1579 g/mol calculated from the elastic moduli at 106 °C.
Control compound MGP-HI were prepared by reacting MGP with HI catalyzed by Zn(OAc)$_2$ in DMF at 60°C for 48 hrs. A molar ratio of MGP: HI = 1:4 was used, and Zn(OAc)$_2$ was added by 1% (w/w). The resulting compound was precipitated and washed with water and ethanol, then was dried in vacuum oven at 60°C for overnight. Control compound PEG-HI was prepared in a similar manner with a molar ratio of PEG:HI=1:2 using a 4:1 mixture of THF and DMF as the solvent. The final product was directly dried at 60°C in vacuum without washing.

Scratches of specimen were created with precisely controlled dimensions using custom built computerized Micro-Cut Instrument that facilitates control of the depth, speed and load during damage. In a typical experiment, a speed of 5 mm/s was utilized. For spectroscopic analysis, the depth of the scratches is controlled to be 100 μm, and for shape recovery analysis, the depth of the cuts is 600 μm. Optical images were recorded using Leica DM2500 M microscope.

Raman imaging were recorded using a Renishaw inVia Raman microscope equipped with a computer controlled three-axis encoded (X, Y, Z) motorized stage, a RenCam CCD detector, and a Leica microscope (DM2500 M). The 785 nm diode laser at 30mW power provided an excitation source. Raman imaging were collected from 27 × 25 μm$^2$ area with spatial resolution of 1 μm$^2$. An acquisition time of 60 sec was used.

Micro-attenuated total reflectance Fourier transform infrared spectra (μATR FT-IR) were performed in the same procedure as described in Section 2.2 of Chapter 2.

Dynamic mechanical analysis (DMA) were performed on a TA Instrument Q800 DMA. Rectangular specimens having a size of ~15.5 mm×6 mm×1 mm were tested at a
frequency of 30 Hz and 5 μm amplitude. Dynamic mechanical properties were measured from -70°C up to 150°C while heating at 2°C/min. Dynamic moduli and mechanical damping (tan δ) were analyzed using TA Universal Analysis 2000. The measured glass transition temperature (T\text{g}) for MGP-PUR at maximum tan δ is 56 ± 1°C. Tensile stretch test was carried out on Instron 4502 at room temperature (20 °C) at a rate of 3 mm/min.

3.3 Results and Discussion

3.3.1 Self-healing of MGP-PUR-Zn(OAc)\textsubscript{2} networks

The synthesis of the crosslinked network is illustrated in Figure 3.1, A, where MGP, and polyethylene glycol (PEG, M\text{w}=300 g/mol) were reacted with hexamethylene diisocyanate crosslinker (HDI) in the presence of Zn(OAc)\textsubscript{2} (1.2% w/w). The following molar ratios of MGP/PEG = 1/1.7 and NCO/OH = 1:1 were used to achieve fully crosslinked networks with the glass transition temperature (T\text{g}) of 56°C (Figure B-1 of Appendix B), the Young’s modulus of 77.8 MPa at 20°C, and the molecular weight between crosslinks (M\text{x}) of 4737 g/mol.

When such MGP-PUR-Zn(OAc)\textsubscript{2} network was cut into two separate pieces and physically reattached, self-healing occurred at 75°C. This is illustrated in Figure 3.1, B. The recovery of the mechanical strength was determined by measuring the tensile stress as a function of the time allowed for self-repair. As shown in Figure 3.1, C, after 72 hrs (3 days), the tensile stress recovery was 5.99 MPa at 80.1% strain (curve a), and reached 9.23 MPa and 162% strain after 7 days (curve b). Extending the recovery time further does not significantly impact tensile strength and strain. Compared to undamaged MGP-PUR-Zn(OAc)\textsubscript{2} networks with a tensile strength of 22.8 MPa, ~40% of tensile strength
was recovered. However, the tensile strength recovery is temperature dependent. At 40°C, only 1.75 MPa of tensile strength was recovered after 7 days. At 20°C, no repairs are observed. It should be noted that the ability of MGP-PUR-Zn(OAc)₂ to recover 9.23 MPa tensile strength is significantly greater compared to the majority of the reported polymers[138] and the recovery to the original shape occurs without melting. For comparison, neat polyurethane crosslinked in the presence of Zn(OAc)₂ (PUR-Zn(OAc)₂) (without MGP), exhibits no self-healing despite of the lower Tₘ (3°C).

Figure 3.1. A - Synthesis of MGP-PUR-Zn(OAc)₂ networks composed of methyl α-D-glucopyranoside (MGP), polyethylene glycol (PEG), and HDI trimer crosslinker; B - Optical images of self-healing at 75°C of MGP-PUR-Zn(OAc)₂ networks; C – Stress-
strain curves of MGP-PUR-Zn(OAc)$_2$ films after healing at 75°C for 3 (a) and 7 days (b). For reference, curve c was recorded from undamaged film.

The stoichiometric ratio of MGP and PEG are varied from 0.28/1 to 0.73/1 as shown in Table 3.1. It shows that higher concentration of MGP not only leads to higher modulus, but also results in higher ultimate stress and strain upon repair. The increase of modulus can be attributed to higher crosslink density and the rigidity of pyranoside ring compared to PEG chains. The increased self-healing efficiency indicates the role of MGP in facilitating the self-repair. However, when the amount of MGP reaches a level causing insufficient chain mobility, self-healing ability is diminished. Concentrations of Zn(OAc)$_2$ in MGP-PUR were varied from 1.2 to 8.4% (w/w). As its concentration increased, self-healing efficiency decreased. This is shown in Table 3.2. The tensile stress after repair decreased significantly when concentration of Zn(OAc)$_2$ is increased from 1.2% to 3.6% (w/w). When Zn(OAc)$_2$ concentration levels are 8.4% (w/w), MGP-PUR does not self-heal. The T$_g$ of Zn(OAc)$_2$-catalyzed MGP-PUR films increases from 57.6 to 60.4°C, as concentration of Zn(OAc)$_2$ increases from 1.2% to 8.4% (w/w). Their corresponding storage moduli at healing temperature (75°C) increases from 3.9 to 6.9 MPa, while the loss modulus increases from 2.6 to 4.5 MPa. Although the T$_g$ difference is only ~3 °C, slight variations in chain mobility at the repairing temperature due to Zn coordination is the determining factor responsible for self-repairing efficiency.
Table 3.1. MGP/PEG ratios utilized to synthesize each specimen, their corresponding Young’s moduli (G), and ultimate strain (ε)/stress (σ) of undamaged and after healing at 75 °C for 7 days obtained from the stress-strain curves.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>MGP/PEG molar ratio</th>
<th>G (MPa)</th>
<th>ε after repair (%)</th>
<th>σ after repair (MPa)</th>
<th>ε of undamaged specimen (%)</th>
<th>σ of undamaged specimen (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MGP-PUR-Zn(OAc)$_2$-a</td>
<td>0.28/1</td>
<td>4.18</td>
<td>70.2</td>
<td>1.24</td>
<td>276</td>
<td>9.50</td>
</tr>
<tr>
<td>MGP-PUR-Zn(OAc)$_2$-b</td>
<td>0.44/1</td>
<td>29.6</td>
<td>82.9</td>
<td>5.03</td>
<td>289</td>
<td>13.3</td>
</tr>
<tr>
<td>MGP-PUR-Zn(OAc)$_2$</td>
<td>0.59/1</td>
<td>77.8</td>
<td>162</td>
<td>9.23</td>
<td>285</td>
<td>22.8</td>
</tr>
<tr>
<td>MGP-PUR-Zn(OAc)$_2$-c</td>
<td>0.73/1</td>
<td>344</td>
<td>4.00</td>
<td>4.49</td>
<td>298</td>
<td>35.5</td>
</tr>
</tbody>
</table>

Table 3.2. MGP-PUR-Zn(OAc)$_2$ networks with various concentrations of Zn(OAc)$_2$ catalyst with their corresponding glass transition temperatures (T$_g$), storage and loss moduli at 75 °C, and tensile stress after repairing at 75 °C for 7 days.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Concentration of Zn(OAc)$_2$ (w/w%)</th>
<th>Glass Transition Temperature (T$_g$)</th>
<th>Storage modulus at 75°C (MPa)</th>
<th>Storage modulus at 75°C (MPa)</th>
<th>Tensile stress after repair (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MGP-PUR-Zn(OAc)$_2$-1</td>
<td>1.2</td>
<td>57.6</td>
<td>3.9</td>
<td>2.58</td>
<td>9.23</td>
</tr>
<tr>
<td>MGP-PUR-Zn(OAc)$_2$-2</td>
<td>3.6</td>
<td>58.3</td>
<td>5.31</td>
<td>3.28</td>
<td>1.48</td>
</tr>
<tr>
<td>MGP-PUR-Zn(OAc)$_2$-3</td>
<td>6</td>
<td>58.4</td>
<td>5.44</td>
<td>3.30</td>
<td>0.95</td>
</tr>
<tr>
<td>MGP-PUR-Zn(OAc)$_2$-4</td>
<td>8.4</td>
<td>60.4</td>
<td>6.9</td>
<td>4.56</td>
<td>0</td>
</tr>
</tbody>
</table>
3.3.2 Spectroscopic analysis of the self-healing mechanism

To set the stage for the analysis of molecular events responsible for damage-repair cycle using Raman and ATR FTIR spectroscopy, Figure 3.2 illustrates optical images of scratched (A) and repaired (A’) MGP-PUR-Zn(OAc)_2 networks. While Raman images of damaged (A) and repaired (A’) areas recorded with 1 μm² spatial resolution are shown in Figure 3.2, B and B’, the corresponding spectra collected inside (area 1/1’ of Figure 3.2, B/B’) and outside (area 2/2’ of Figure 3.2, B/B’) scratch are shown in Figure 3.2, C/C’, Traces 1/1’ and 2/2’. The color scale represents the Raman intensity distribution of the 1756 cm⁻¹ band. The Raman spectra were normalized to the 1440 cm⁻¹ band, which is attributed to asymmetric C-H deformation vibration of the aliphatic segments. Table B-1 of Appendix B provides detailed tentative band assignments. Upon damage, the C-H and C-C band intensities associated with -N at 1328 and 1067 cm⁻¹ increases with respect to the C-H and C-C vibrations associated with -O at 1285 and 1036 cm⁻¹. These changes are attributed to the cleavage of urethane linkages (NHC(O)O), and there are two possible mechanisms. If cleavages occur at urethane (O)C-N bond, generating –R-O-(O)C∙ and –R–NH∙ radicals, upon releasing of CO₂ and H abstraction, –CH₃ (or –CH₂-) and –R-NH₂ are formed at the cleaved chain ends. If cleavages occur at urethane O-C(O) bond, –R-N-(O)C∙ and –R–O∙ are generated. The former may be converted into –R-NH₂ by reaction with H₂O at the presence of catalyst, releasing CO₂, whereas the latter leads to the formation of -R–OH groups. Based on spectroscopic data, the two mechanisms will lead to the formation of -NH₂ groups The decrease of C=O vibration of HDI trimer ring (1756 cm⁻¹), increase of symmetric deformation vibration of aliphatic C-H (1305 cm⁻¹), as well
as decrease of aliphatic C-C vibrational bands (1094 cm\(^{-1}\)) are attributed to either cleavage or conformational changes of the HDI trimmer segments upon mechanical damage. As shown in Traces 1’ and 2’ in Figure 3.2, C’, after repair, no spectroscopic changes are observed in the repaired area which is likely attributed to the Raman detection limits. Therefore, further analysis will be conducted using ATR FTIR.

Figure 3.2, D illustrates ATR FTIR spectra collected from damaged (Traces a) and undamaged (Trace b) areas of MGP-PUR-Zn(OAc)\(_2\). Trace c is the subtraction of Traces (a – b), which amplifies the detected intensity changes. The results of the same analysis performed after self-repair are shown in Traces a’ (repaired), b’ (undamaged), and c’ (subtraction trace) of Figure 3.2, D’. Upon damage, the decrease of the C=O at 1680 cm\(^{-1}\) (Figure 3.2, D, Trace c) and C-N at 1243 cm\(^{-1}\) bands due to urethane linkages are observed, indicating cleavage of NHC(\(\text{O}\))O bonds. Furthermore, the increase of the 1081 and 1005 cm\(^{-1}\) bands due to C-OH vibrations are attributed to MGP-OH formation, which again, results from NHC(\(\text{O}\))O cleavage. The net result is the generation of –NH\(_2\) groups upon mechanical damage manifested by the appearance of the band at 1627 cm\(^{-1}\) due to N-H vibrations. Also, H-bonding dissociation was observed manifested by the slight increase of non-H-bonded C=O vibrations at 1710 cm\(^{-1}\). Thus, after mechanical damage, cleavage of urethane linkages and H-bonding occur, which leads to the formation of –NH\(_2\) and MGP-OH functional groups.
Figure 3.2. A – Optical image of MGP-PUR-Zn(OAc)$_2$ film immediately after damage; B – Raman imaging of the area shown in Figure 3.2, A; The color scale represents intensity distribution of the 1756 cm$^{-1}$ band; C - Traces 1 and 2 are the Raman spectra collected from inside (area 1) and outside (area 2 marked in Figure B) damaged area; The band at 1756, 1094 and 1067 cm$^{-1}$ are enlarged and shown in the inserts for visual effects; D - Traces a and b are the ATR-FTIR spectra collected from severely damaged and undamaged MGP-PUR-Zn(OAc)$_2$ films, respectively. Trace c is the subtraction spectrum
a-b; A’ – Optical image of MGP-PUR-Zn(OAc)$_2$ film after self-healing at 75°C for 7 days; B’ – Raman imaging of the area shown in Figure 3.2, A’. The color scale represents intensity distribution of the 1756 cm$^{-1}$ band; C - Traces 1’ and 2’ are the Raman spectra collected from inside (area 1’) and outside (area 2’ marked in Figure B’) damaged area; D’ - Traces a’ and b’ are the ATR-FTIR spectra collected from repaired and undamaged areas MGP-PUR-Zn(OAc)$_2$ film after repairing at 75°C for 7 days. Trace c’ is the subtraction spectrum a’-b’.

The analysis of MGP-PUR-Zn(OAc)$_2$ networks upon self-repair is shown Figure 3.2, D’. IR bands responsible for the urethane free C=O, H-bonded C=O stretching, N-H deformation, C-N stretching, and C-O-C stretching vibrations at 1715, 1680, 1527, 1243, 1150, and 1045 cm$^{-1}$, respectively, decrease (Trace c’). However, the bands at 1633, 1562, 1270, and 1081 cm$^{-1}$ due to C=O stretching, N-H deformation, C-N stretching, and C-O-C stretching vibrations characteristic of urea bonds, increase. These observations indicate urethane-to-urea conversion during repair, which is further magnified by doubling the amount of urea linkages after 7 days at 75°C in comparison to a 3-day repair. As anticipated, when the temperature is lowered to 40 °C, significantly less urea is formed (Figure 3.3, A). In contrast, urea formation does not occur for the same PUR-Zn(OAc)$_2$ networks without MGP (Figure 3.3, B) which lead to the question of the role of MGP molecules during self-repair.
Figure 3.3. A - ATR-FTIR spectra of repaired (Trace a) and undamaged (Trace a’) Zn(OAc)$_2$ catalyzed MGP-PUR after exposure to 40°C for 7 days. Trace a” is the subtraction spectrum of Trace a-a’. B – ATR-FTIR spectra of repaired (Trace b) and undamaged (Trace b’) Zn(OAc)$_2$ catalyzed PUR after exposure to 75°C for 7 days. Trace b” is the subtraction spectrum of Trace b-b’.

3.3.3 Reactivity of MGP-Urethane linkages

The presence of MGP in MGP-PUR-Zn(OAc)$_2$ networks generate urethane linkages in C2, C3, and C4 positions of MGP labeled in Figure 3.1, A. These MGP-urethanes linkages exhibit reduced stability due to their secondary carbon-oxygen bond and the presence of bulky pyranoside groups.[139] Thus, the urethane carbonyl groups of these moieties are more reactive toward nucleophiles. Therefore, the –NH$_2$ and –OH generated at damaged sites, as identified by spectroscopic analysis, are responsible for the reactions with MGP-urethanes in the presence of Zn(OAc)$_2$ catalyst, and lead to the
formation of urea linkages. To examine this hypothesis, a model molecule was synthesized by reacting MGP with hexyl isocyanates (HI) to generate MGP-urethane linkages. In turn, these molecules were reacted with a diamine, 2,2’-(ethylenedioxy)bis(ethylamine) (EDBEA) catalyzed by Zn(OAc)$_2$ under various temperatures.

The ability of Zn(OAc)$_2$ to catalyze MGP-PUR networks self-repair is predominantly determined by the susceptibility of urethane bonds toward nucleophiles, such as $–$NH$_2$ or $–$OH groups. Three control compounds were synthesized. They are shown in Figure 3.4. Compound MGP-4HI was synthesized by reacting one MGP molecule with 4 equivalent amount of HDI, representing the urethane linkages associated with MGP (MGP-urethane) in the network. Note, the urethane in C6 position of MGP has less steric hindrance compared to their counterparts in C2, C3, and C4 positions. Thus, C6 urethane maybe more stable, which is examined using compound MGP-1HI. PEG-2HI has the same structural elements as the urethane segments associated with PEG within MGP-PUR-Zn(OAc)$_2$ network.
Figure 3.4. Synthesis of control compounds MGP-4HI, MGP-1HI, and PEG-2HI.

To examine reactivity of MGP-4HI compound with nucleophiles, MGP-4HI was first reacted at 75°C with the diamine compound EDBEA. ATR-FTIR spectra were recorded after 1, 5, 24, and 48 hrs of reaction to follow any change of the urethane bonds. The results are shown in Figure 3.5, A, which illustrate intensity decreases of the urethane bands at 1698 and 1550 cm\(^{-1}\) as well as new bands formation at 1620 and 1596 cm\(^{-1}\). The 1620 cm\(^{-1}\) band is due to urea C=O vibrations, while the band at 1596 cm\(^{-1}\) is attributed to N-H vibrations of \(-\text{NH}_2\). When the same reaction was carried out at 40 °C, only a small of amount urea was produced after 48 hrs of reaction, as manifested by the formation of a weak band at 1620 cm\(^{-1}\). This is shown in Figure 3.5, B. When MGP-4HI was reacted with EDBEA without Zn(OAc)\(_2\), no reaction occurred after 48 hr at 75 °C. This is shown in Figure 3.5, C, where the urethane bands at 1698 and 1550 cm\(^{-1}\) did not
change intensities, and the formation of urea linkages was not observed. The reactivity of MGP-urethanes toward OH groups at the presence of Zn(OAc)$_2$ were also examined as shown in Figure 3.5, D. No reaction occurred within 48 hrs. Therefore, urethane bonds associated with MGP alone are thermally stable, but are able to react with $-$NH$_2$ when catalyzed by Zn(OAc)$_2$ at 75°C, generating urea linkages.
Figure 3.5. Figure A – D illustrates ATR-FTIR spectra of MGP-4HI reacted under the following conditions: A1 – MGP-4HI react with EDBEA catalyzed by Zn(OAc)$_2$ at 75°C; A2 – MGP-4HI react with EDBEA catalyzed by Zn(OAc)$_2$ at 40°C; A3 – MGP-4HI react with EDBEA at 75°C without Zn(OAc)$_2$; A4 – MGP-4HI react with butanediol catalyzed by Zn(OAc)$_2$ at 75°C. For each reaction, four ATR-FTIR spectra were collected after 1, 5, 24, and 48 hrs of reaction.

Although 80% of the urethanes bonds of MGP-4HI are reacted with amine groups after 48 hrs, as shown in Figure 3.5, A, reactivity of the urethane in the C6 position of MGP is unclear. Thus, MGP-1HI was synthesized and reacted with EDBEA at 75°C in the presence of 1.2% (w/w) Zn(OAc)$_2$. Decomposition of urethane linkages was observed, as shown in Figure 3.6, A, and manifested by the decrease of the 1698 cm$^{-1}$ band. ATR-FTIR spectra of PEG-2HI reacted with EDBEA catalyzed by Zn(OAc)$_2$ at 75°C is shown in Figure 3.6, B. No reaction has occurred. These results identified the reaction shown in Figure 3.7 is responsible for formation of urea from reaction of –NH$_2$ with MGP-urethanes.
Figure 3.6. A – ATR-FTIR spectra of MGP-1HI reacted with EDBEA catalyzed by Zn(OAc)$_2$ at 75°C; B – ATR-FTIR spectra of PEG-2HI reacted with EDBEA catalyzed by Zn(OAc)$_2$ at 75°C. For each reaction, four spectra were collected after 1, 5, 24, and 48 hrs of reaction.

Figure 3.7. Proposed reaction of the model compound MGP-4HI with EDBEA catalyzed by Zn(OAc)$_2$ at 75 °C.

When MGP-4HI is reacted with EDBEA, as the concentration of Zn(OAc)$_2$ increases from 0 to 8.4% (w/w), dissociation rate of MGP-urethane bonds at 75°C
increased, as shown in Figure 3.8. However, reaction kinetics in the solid state is different, and is dominated by diffusivity of reactants. This is reflected in Table 3.2 where the self-healing efficiency decreases as concentration of Zn(OAc)$_2$ within MGP-PUR-Zn(OAc)$_2$ network increases.

![Graph](image)

**Figure 3.8.** Relative IR intensity of urethane C=O vibrational band of MGP-4HI at 1698 cm$^{-1}$ when MGP-4HI was reacted with EDBEA at 75°C for 5 hrs plotted as a function of Zn(OAc)$_2$ concentrations.

The results of these experiments showed that the urethanes linked to MGP react with –NH$_2$ groups to form urea linkages in the presence of Zn(OAc)$_2$ at 75°C. Notably, these reactions do not occur without Zn(OAc)$_2$, or by replacing -NH$_2$ with -OH. The reaction rates are significantly lower at 40°C. It should be noted that the PEG-urethane compounds synthesized by reacting PEG with two equivalent amounts of hexyl
isocyanates are unreactive toward -NH₂ under the same conditions, indicating that PEG-urethane linkages exhibit enhanced stability compared to the MGP-urethanes.

3.3.4 Proposed self-healing mechanism

In view of these experimental data, the following self-healing mechanism for MGP-PUR-Zn(OAc)₂ networks is elucidated. Upon mechanical damage, urethane bond cleavage and the dissociation of H-bonding are the primary events. When two surfaces resulting from mechanical damage are physically re-attached due to stored entropic energy, H-bonds are reformed, facilitating initial interfacial re-bonding. Although the strength is relatively weak, it is critical at this stage to maintain interfacial connectivity before sufficient quantities of covalent bonds are reformed. Also, indirect evidence suggests that when two physically reattached surfaces are exposed to 110°C, they become detached, suggesting that the H-bonding (5-10 kcal/mole; ~110-120°C) could be responsible for reattachment at the early stages of self-healing at 75°C. Covalent re-bonding manifested by the urethane-to-urea conversion, as shown in Figure 3.9, A, is responsible for the recovery of mechanical strength at the repaired interfaces. When temperature is increased to 75°C, the –NH₂ groups generated during damage react with MGP-urethane bonds through nucleophilic attack, whereby Zn(OAc)₂ catalyzes the reaction by activating carbonyl groups via metal-ligand coordination. As a result, cleaved chains are re-connected by urea linkages (Figure 3.9, A). This process is also schematically depicted in Figure 3.9, B. It should be noted that since primary amine groups are generated by mechanical damage, and are not present in the undamaged networks, thermal stability of undamaged material is unaffected. Thermogravimetric
analysis (TGA) show 2% weight loss at 243°C (Figure B-2 of Appendix B). Notably, further increased Zn(OAc)₂ concentration levels compromise the repair efficiency due to strong coordination between Zn - polar sites, thus limiting chain mobility as is discussed in Table 3.2.

**Figure 3.9.** A – Proposed mechanism responsible for thermal healing of Zn(OAc)₂-catalyzed MGP-PUR; B – Schematic illustration of re-connection of cleaved chains at the area of damage via PUR-to-PUA conversion.

3.4 Conclusions

Living organisms utilize metabolic processes to achieve adaptive, reproductive, and self-healing functions, which require dynamic and precise control of sequential chemical events. Among chemical reactions involved in metabolism, amine
functionalities are perhaps the most prevalent reactive groups responsible for maintaining living functions at cellular and organ levels. Deliberately modified with methyl α-D-glucopyranoside (MGP) and catalyzed by zinc acetate (Zn(OAc)$_2$), polyurethane (PUR) networks are capable of generating primary amines upon mechanical damage as a result of covalent bond cleavages. In turn, the damage-induced amines are able to react with network urethane groups to reform covalent linkages, thus restore mechanical properties upon mechanical damage.
4.1 Introduction

Self-healing is driven by physical and/or chemical events regardless of the various mechanisms. For chemical reactions leading to re-bonding to occur, there are two pre-requisites: (i) reactive groups on two mechanically separated surfaces must be physically brought into contact with each other and (ii) reactivity of these groups must lead to re-bonding. While chapter 2 and 3 illustrated reactions that lead to re-bonding of cleaved chain ends, what is the physical driving force for self-healing?

Initial studies on thermoplastic polymers suggested that the primary driving force for repairs is chain diffusion at the polymer-polymer interface that forms chain entanglements,[6] and reptation model[140, 141] was utilized to semi-quantified these events by describing the motion of macromolecular segments trapped in a stationary tube[142]. Self-healing is achieved only when the entire chain completely disengaged from the “tube”, reaching equilibrium state after a given time. Along the same line, majority of studies utilized dissociation of covalent or non-covalent bonds under stimuli to induce macroscopic flow to heal damages, which is shown in Figure 4.1, A. One of our previous work involving PUR networks modified with oxetane/oxolane-substituted chitosan demonstrated that scratch recovery is driven by a flow of fragmented network components to form a scar.[42, 43] For thin films coated on a substrate, the healing is illustrated as a surface tension driven viscoelastic flow.[36] However, these materials are either soft or require repair temperature significantly above the glass transition ($T_g$) or
melting temperature ($T_m$). Taking a different approach, if shape memory materials that “remember” their shape before damage are utilized, their presence may be advantageous in designing self-healing polymers.

The primary advantage of using shape memory materials in self-healing is driven by an opportunity to close a crack, as is shown in Figure 4.1, B. When a polymer network is deformed, by applying a stimulus, shape memory components can exert a recovery force to minimize the size of the crack. One attempt to achieve this is by embedding pre-tensioned shape-memory alloy (SMA) wires into self-healing epoxy with manually injected[143] or microencapsulated healing agent[144]. But, alignment of the wires is required. Perhaps the most practical approach is to utilize bulk shape memory polymers (SMP). Traditional definition for SMP is that when polymers are plastically deformed while exposed to temperatures above thermal transitions, such as $T_g$, $T_m$, or liquid crystalline ($T_{LC}$) transitions, upon cooling, the temporary shape will be retained. Upon heating above the transition again, the original shape will be recovered. Thus, shape memory polymers (SMP) are capable of storing temporary and recovering permanent shapes upon thermal exposure or other stimuli. In order for a polymer to exhibit SME, the first requirement is to have junction points, such as chemical crosslinks, physical entanglements, or both, which inhibit chain slippages during deformation and allow for storage of energy. This is responsible for the elastic behavior of the polymer. The second requirement is to have molecular switches that are sensitive to the external stimulus in order to fix the temporary shape [145, 146]. The switches can be achieved by utilizing vitrification/$T_g$, or crystallization/$T_m$, reversible crosslinks, or other temporary
interactions to fix the temporary shape by changing molecular mobility [147-149]. The shape recovery is driven by elasticity of the material. Examples include a polystyrene based shape memory thermosetting polymer blended with 6% by volume copolyester thermoplastic particles which is able to repair at 150 °C for 20min,[150] and crosslinked poly(ε-caprolactone) (n-PCL) network interpenetrated with linear poly(ε-caprolactone) (l-PCL) which can be repaired by heating above T_m [151]. Or using electro-spun thermoplastic poly(ε-caprolactone) fibers which were randomly distributed in shape-memory epoxy matrix, featuring flow of fibers upon heating to rebond the crack besides the shape memory effect.[152]

**Figure 4.1** Schematic illustration of two types of physical processes involved in self-healing: A – an interfacial flow causes damages repair; B – the presence of shape memory components, where elastic forces of spring-like polymers force the closure of damage.
The practicality of the SMP based self-healing systems comes from the fact that the shape recovery may occur rapidly at temperatures within or little above the glass transition or a predesigned transition temperature $T_S$, thus $T_g$ and $T_m$ of the material can be tuned to higher temperature compared to polymer flow based self-healing, and the original shape can be recovered without re-shaping. Despite the advantages, however, the role and enormous potential of SMP in facilitating self-healing has not been fully addressed. This section of the study will show that self-healing for monosaccharide modified PUR network is facilitated by the shape memory effect (SME) enhanced mobility at a damaged area, which leads to subsequent bond formations.

It should be noted that, it is known but not yet being widely realized that, in fact, the majority of polymers do exhibit SME. Thus, one should note that there are a large variety of polymers that can be used in designing self-healing materials, and a simple universal method of detecting their SME is necessary. Traditionally, shape memory has been detected by thermo cycles, and iso-strain experiments and thermomechanical cycles have been utilized to quantify the SME. However, there is no simple universal method to identify SME and the temperature at which SME occurs. In this study, it is discovered that unique shape memory transitions ($T_{SM}$) can be observed utilizing dynamic mechanical analysis (DMA), macroscopically manifested by sample length changes in the $T_g$ region. Using this approach, information about polymer architecture and viscoelastic properties can be obtained, allowing shape memory in polymers to be predicted from a single DMA experiment.
4.2 Experimental Methods

MGP-PUR-Zn(OAc)$_2$ films are utilized for this study. Their synthesis is described in Section 3.2 of Chapter 3. MGP-PUR-DBTDL network exhibits similar mechanical properties. Scratches of controlled dimensions are generated according to the method described in Section 2.2 of Chapter 3. Tensile stretch test was carried out on Instron 4502 at room temperature (21 °C) at a rate of 3 mm/min.

Polytetrahydrofuran (PTHF, Avg. MW=650g/mol) based glycerol crosslinked polyurethane films (PTHF-PUR) were prepared by first reacting 1 mol glycerol with 2.27 mol IPDI catalyzed by 6.43×10$^{-3}$ mol DBTDL in THF (75% solid (v/v) solids) at 55 °C for 10 minutes. Then 2.78 mol of PTHF (avg. Mw = 250) and additional 2.27 mol IPDI were added to the pre-polymer solution. After complete mixing, the solution was applied to glass substrate. The films were cured at room temperature for overnight followed by heating at 110 °C for 24 hrs. Polycaprolactone (PCL, avg MW=4000 g/mol) based polyurethane (PCL-PUR) was synthesized by first reacting PCL (1.25 g) with HDI (48 μL) in THF (1.5 ml) catalyzed by DBTDL (2 μL) at 70 °C for 30 mins, forming solution A. Then dissolve 1,4-BD (0.058 g) and HDI (113 μL) in THF (0.4 ml) and add the solution into solution A, and continue to react at room temperature for 10 mins until the solution became opaque. PUCL fibers were drawn from the solution at room temperature and dried at 50 °C for 24 hrs.

Dynamic mechanical analysis (DMA) was performed on a TA Instruments Q800 DMA in strain control mode. Rectangular film samples with dimensions of 40×5 ×1 mm were tested using 10 μm amplitude, force track 125%, at 10 Hz, from 5⁰C up to 120⁰C at
2°C/min, and 10 mm testing length as standard conditions. Dynamic moduli, mechanical
dampening, and length were analyzed using TA Universal Analysis 2000.

The shape recovery process was performed in strain control mode on TA Instruments Q800 DMA, using 10 μm amplitude, frequency 10 Hz, and force track 125% throughout. Dimension of the film is 7.62×2.70×0.15 mm. For the standard dual-shape memory cycle, a preload force of 0.025 N was first applied while the temperature was equilibrated at 75 °C and held isothermally for 8 mins. Then the static tensile force is ramped to 0.26 N at a speed of 0.26 N/min, after which, temperature was dropped to -40°C at 20 °C /min, and then held isothermally for 18 minutes. The static force was then removed. Only the 0.025 N preload force was applied. Next, the temperature was increased at 5 °C /min to 75 °C and again held isothermally for 25 minutes to complete the recovery process. Room temperature shape deformation followed by shape recovery cycle was performed on a MGP-PUR-Zn(OAc)$_2$ film of 7.32×2.25×0.2 mm. Temperature was first equilibrated at 21 °C and a preload force of 0.014 N was applied. Then the force was ramped to 8.57 N at a speed of 8.57 N/min at 21 °C and kept isothermally for another 2 mins. Then force was then dropped to 0.014N and temperature was held at 21 °C for 15 mins. The temperature was then increased to 75 °C at 5 °C/min until completion of the recovery process.

4.3 Results and Discussion

4.3.1 Effects of shape memory effects (SME) in self-healing of polymers

For self-healing materials that are mechanically damaged, the deformed areas should automatically recover to their original shapes. This physical process is monitored
for MGP-PUR-Zn(OAc)$_2$ network, where the closure of a 75 μm (width) × 600 (depth) μm scratch is recorded as a function of time. This is shown in Figure 4.2, A, which exhibits elasticity driven shape recovery. The recovery takes ~10 min at 21 °C, but when the temperature is raised > 40 °C, the recovery takes < 10 sec. Such shape recovery effect is governed by the rubber elasticity of the network at or above the glass transition temperature ($T_g$), and is driven by the recovery of the entropic network energy stored during mechanical deformation.[157] Figure 4.2, B illustrates the elasticity of MGP-PUR-Zn(OAc)$_2$ networks upon 80% strain at 21 °C, which within ~20 s recovers the original length at temperatures above 40 °C, but the same process takes ~5 hrs at 21 °C. This behavior can also be described as shape memory effects (SME).

**Figure 4.2.** A – Recovery of a 75×600 μm (width×depth) cut as a function of time at 20 °C (film thickness is 1mm). The optical images are taken from the side section of the cut; B - Recovery of MGP-PUR-Zn(OAc)$_2$ film after being elongated by 80% at 20 °C; C – Maximum tensile force of MGP-PUR-Zn(OAc)$_2$ after being cut by 75×600 μm at the
center of the film, healing the cut at 20 °C and 75 °C for 7 days; D – Schematic illustration of the sequential physical and chemical events responsible for self-healing of MGP-PUR-Zn(OAc)₂ network.

To further demonstrate the SME of MGP-PUR-Zn(OAc)₂, a standard dual shape memory cycle (SMC) [153] was performed using dynamic mechanical analysis (DMA) which is shown in Figure 4.3. To briefly describe the cycle, X axis is the time of the experiment, while the force and temperature applied to the specimen are shown on Y1 and Y2, the resulting length changes are plotted on Y3 axis. At 75 °C, a force is applied to stretch the film until it reached 15.6% of strain. While the force is applied, temperature is dropped to -40 °C to fix the shape. Then the force is removed and temperature is increased to 75 °C over a period of 20 mins. The length of the specimen does not change significantly until the temperature reaches 39 °C, when length recovery starts. The materials ability to fix the temporary shape at certain temperature is defined by shape fixing ratio (R_f), which is defined as:

$$R_f = \frac{\varepsilon_f}{\varepsilon_{max}} \times 100\%$$  \hspace{1cm} (1)

where $\varepsilon_{max}$ is the maximum strain reached upon deformation at elevated temperature, and $\varepsilon_f$ is the strain reached after load removal and shape fixation. The efficiency of shape recovery is defined by the shape recovery ratio (R_r), and is calculated by the following equation

$$R_r = \frac{(\varepsilon_f - \varepsilon_r)}{\varepsilon_f} \times 100\%$$  \hspace{1cm} (2)
where $\varepsilon_r$ is the strain after shape recovery. The $R_f$ value of the SMC shown in Figure 4.3 is 98%, and the $R_r$ is 90%. It should be noted that $R_f$ and $R_r$ values are dependent on experimental conditions including the deformation temperature, recovery temperature, and maximum strain.

The shape memory cycle shown in Figure 4.2, B is also performed on DMA to semi-quantify the SME under such conditions, and the results are shown in Figure 4.4. At 21 °C, the tensile force is applied and the specimen is stretched to 214% of strain. After removal of the strain, the specimen contracts rapidly, but the contraction becomes significantly slower when it reaches 110% strain, corresponding to the slow recovery shown Figure 4.2, B when carried out 21 °C. When the temperature increases again, the speed of length recovery starts to increase at 25 °C, and reached the steady state when temperature is increased to 63 °C. This cycle was repeated four times with varying static force so that different $\varepsilon_{\text{max}}$ is obtained. The corresponding $\varepsilon_r$ is plotted for each $\varepsilon_{\text{max}}$, which is shown in Figure 4.4, B and the values are listed in the Table of Figure 4.4, C. A linear relation is obtained where $\varepsilon_r = 0.14\varepsilon_{\text{max}}+5.62$. The intercept on Y axis is attributed to thermal expansion as temperature increases from the 21 °C to 75 °C. There is no shape fixation step for this specific cycle, its shape recovery ratio ($R'$) is calculated by

$$R' = \frac{\varepsilon_{\text{max}}-\varepsilon_r}{\varepsilon_{\text{max}}} \times 100\% \quad (3)$$

After deducting the thermal expansion from $\varepsilon_r$, $R'$ values are calculated from the adjusted $\varepsilon_r$ and $\varepsilon_{\text{max}}$. They are plotted in Figure 4.4, B and listed in Figure 4.4, C. Variation of $R'$ with $\varepsilon_{\text{max}}$ is relatively small, and the shape recovery ratio $R'$ is $85.76\pm0.50\%$. 

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When deformation occurred at 75 °C for traditional dual-shape memory cycle shown in Figure 4.3, upon cooling, 98% of shape fixity is reached at 20 °C. No significant shape recovery was observed until the temperature reached 39 °C. However, when deformation was performed at 20 °C, at the same temperature, upon removal of load, the length immediately contracted as shown in Figure 4.4. The lack of shape fixity in the second experiment is no surprising. MGP-PUR-Zn(OAc)$_2$ has a broad glass transition from 20 to 90 °C which is due to the high dispersity of molecular weights. The results indicate that the chains being deformed at 75 °C and 15.6% of strain are those with macroscopic mobility at T > 39 °C, and thus no sufficient mobility at 20 °C to initiate shape recovery, resulting in good shape fixity at 20 °C. When deformation occurs at 20 °C, however, which is the onset of glass transition, the chains being elongated are those with certain mobility at this temperature. Upon load removal, when temperature is kept the same, the mobility and entropy driven elasticity of these chains are responsible for the immediate shape recovery.
Figure 4.3. Standard dual-shape memory thermomechanical cycle for MGP-PUR-Zn(OAc)$_2$ with deformation temperature ($T_d$) at 75 °C. Static force, temperature, and length are plotted as a function of time.

To determine how SME along with covalent bond reformations contribute to self-healing, two MGP-PUR-Zn(OAc)$_2$ specimens were partially cut and allowed to self-repair for 7 days at 20 and 75°C without physical reattachment. After that time, tensile measurements were conducted and the results are summarized in Figure 4.2, C. As seen, the specimen repaired at 75 °C requires a load of 63.6 N (9.3 MPa) to rupture. This value matches the rupture force/stress of the completely cut specimen repaired by temporarily pressing damaged sites against each other followed by exposure to 75 °C (Figure 4.1 C, Trace b). For the same specimen kept at 20 °C for 7 days, 50.4 N load is required to
rupture. For reference, a specimen cut without repair ruptures at a load of 38 N. These results indicate that the elastically driven shape recovery facilitating interfacial contact is capable of enabling covalent re-bonding when reactive groups such as primary amines are generated. Taking into consideration the chemical reactions occurred during the self-healing as described in Chapter 3, the sequence of the events responsible for self-healing of MGP-PUR-Zn(OAc)$_2$ is depicted in Figure 4.2, D. Self-repair is initially driven by entropic shape recovery facilitating interfacial contacts in damaged areas, followed by H-bonding and covalent reformation of cleaved bonds.
Figure 4.4. A – Shape memory cycle of MGP-PUR-Zn(OAc)$_2$ with deformation temperature ($T_d$) at 21 °C. Static force, temperature, and length are plotted as a function of time. B – Strain after recovery ($\varepsilon_r$) and shape recovery ratio ($R$) for various maximum strain reached upon deformation ($\varepsilon_{\text{max}}$). C – Corresponding values of $\varepsilon_{\text{max}}$, $\varepsilon_r$, adjusted $\varepsilon_r$ ($=\varepsilon_r - 5.62$), and $R$ as shown in Plot B.

4.3.2 Prediction of shape memory effect from dynamic mechanical analysis

Interestingly, during a normal DMA run of MGP-PUR-Zn(OAc)$_2$ when storage modulus, loss modulus, and tan $\delta$ are measured as shown in Figure 4.5, A, Curves a, b, and c, respectively, it is observed that the specimen length (curve d) increases at the onset of $T_g$ and subsequently contracts back as temperature increases to 39 °C. This temperature is in agreement with the onset temperature for SME during the standard SMC as shown in Figure 4.3. It is hypothesized that the length retraction is an indication of the presence of $T_g$ based SME, as well as prediction for occurrence of shape recovery facilitated self-healing, and this length increase is a result of the molecular architecture and viscoelastic properties of the polymer. To verify this hypothesis, a shape memory
cycle is performed on MGP-PUR-Zn(OAc)\textsubscript{2} network and is illustrated in Figure 4.5, B. The shape fixation process is shown in Figure 4.5, B, a-c, and the recovery process in images d-i. Starting with the initial shape (a), the material is then deformed above the \( T_g \) (b). This temporary shape is fixed by maintaining the deformation while cooling to below the \( T_g \) (c). Shape recovery occurs (e-j) once the temperature is increased to the recovery temperature (\( T_{\text{recover}} \)) above the \( T_g \). The shape recovery time, defined as the time required to complete shape recovery (go from c to j in Figure 4.5, B), is measured for different \( T_{\text{recover}} \), and the result is plotted in Figure 4.5, C. The shape recovery took a significantly shorter time when \( T_{\text{recover}} \) is increased to 39 °C, and a further temperature increase has only a marginal impact. This matches the temperature at which length reaction occurs during DMA measurement as shown in Figure 4.5, A, curve d. Thus, it indicates that the length change observed in DMA is closely correlated with \( T_g \) based SME of polymers, where initiation of significant shape recovery can be obtained.
Figure 4.5 A – Storage (a) and loss (b) moduli, tan delta (c), and length changes (d) of MGP-PUR-Zn(OAc)$_2$ film measured as a function of temperature using dynamic mechanical analysis (DMA); B – the shape memory effect of MGP-PUR-Zn(OAc)$_2$ film as a function of time (films are transparent and color was added for visual effect) with original shape (a), deformed shape at 110 °C (b), fixed shape at 20 °C (c), and shape recovery process at $T_{\text{recover}}$ (d-i); C – the time required for film to recover from the deformed shape (c) to the original shape (a) at various recovery temperatures ($T_{\text{SR}}$).

In order to show the universality of this approach, the same measurements were carried out for a poly(tetrahydrofuran) (PTHF) based polyurethane crosslinked with glycerol (PTHF-PUR) which has a $T_g$ of 40 °C. The result is shown in Figure C-1 of Appendix C, and shows that the temperature at which length retraction occurs matches
the temperature at which shape recovery start to proceed at significantly fast speed. However, for $T_m$ based shape memory polymers, there is no length peak, which will be addressed later.

To illustrate the origin of this behavior, it is worth noting that in a strain-controlled DMA experiment, while a sinusoidal dynamic force ($f_d$) is applied, a static force ($f_s$) is also applied to the specimen, so that the dynamic force is maintained in the material’s tensile region. The $f_s$ changes proportionally to the maximum $f_d$ of each cycle. Therefore, it drops as the temperature increases and material softens, as shown in curve a of Figure 4.6, Trace a. As the temperature approaches the $T_g$ region, the polymer starts to exhibit viscoelastic behavior, indicated by the rise in tan $\delta$. Thus, under the applied dynamic and static force, the length of the specimen starts to increase as a result of increased viscous component (Figure 4.6, Trace b). If the elongation causes chain flow/slippage, no energy is stored and the length will continue to increase as a function of temperature under the applied force. However, MGP-PUR-Zn(OAc)$_2$ networks also exhibit elasticity, where the presence of chemical crosslinks limits the flow/chain slippage. Thus, deformation causes the chains to elongate, resulting in increased order and decrease of their conformational entropy. The theory of polymer elasticity describes the entropy change during uniaxial elongation per volume of material as

$$\Delta S = -\frac{\rho R}{2M_x} \left(\frac{2}{\alpha} + \alpha - 3 \right) \quad (4)$$

where: $\alpha$ is the extension ratio $L/L_0$, $\rho$ is density, $R$ is the gas constant, and $M_x$ is the molecular weight between crosslinks/entanglements. This decrease in entropy upon stretching generates a contractive force, and the associated stress is expressed as
\[ \sigma_R = \frac{\rho RT}{M_x} \left[ \alpha - \frac{1}{\alpha^2} \right] \quad (5) \]

where T is temperature. The entropic contractive force generated as a result of length increase with increasing temperature is calculated from Eqn. (5). The \( \rho \) of MGP-PUR-Zn(OAc)2 network is measured as 1.2 g/cm\(^3\), and \( M_x \) calculated from the E’ at 106 °C (50 °C above \( T_g \)) using \( M_x = \rho RT/E' \) is 4737 g/mol. The result is shown in Figure 4.6, Trace c. The length of specimen is shown in Trace c and illustrates that the length increases as a function of temperature until the contractive force exceeds the applied static force. The former increases as the material is stretched further while the latter decreases as the material softens. When contractive force generated is equal to the applied static force, length contraction occurs.

![Figure 4.6 Static force (f_s) applied to the MGP-PUR-Zn(OAc)_2 film during a DMA run (Trace a), length of the test area (Trace b), and the contractive force generated as a result](image)

**Figure 4.6** Static force (f\(_s\)) applied to the MGP-PUR-Zn(OAc)\(_2\) film during a DMA run (Trace a), length of the test area (Trace b), and the contractive force generated as a result
of lengthening calculated based on Eqn. (2) (Trace c) plotted as a function of the temperature.

The length change is dominated by polymer’s viscoelastic property shifts upon entering the $T_g$ region. It is of interest to induce shape recovery and self-healing within $T_g$ region is due to the polymers’ better mechanical properties than above their $T_g$s. For materials with low crosslink density and high tan $\delta$, larger length increase will be observed as such materials exhibit higher viscous component compared to the elastic component. As shape memory materials, they are able to undergo larger scale of shape deformation without breaking. If recovery of majority of the elongation is observed in DMA, it indicates that the material is able to store the energy and generate sufficient contractive force to induce SME. On the contrary, if the length continues to increase or the length contraction is small, crosslink density of the polymer is too small that the energy is dissipated from change slippages. Therefore, the SME will be limited. On the other hand, for materials with high crosslink density and low tan $\delta$, the drop of $E'$ during glass transition is small, as a result, the length increase in DMA will also be small. One example is the DMA of polycaprolactone (PCL) based semi-crystalline polyurethane (PCL-PUR) which is shown in Figure C-2 of Appendix C. As seen, within its glass transition from -65 °C to -5 °C, $E'$ drop and tan $\delta$ are both very small compared to MGP-PUR-Zn(OAc)$_2$ and PTHF-PUR due to the presence of PCL crystalline phase, the length increase observed is very small without contraction. These materials may exhibit high recovery force and speed when deformed. However, the ability to undergo shape deformation is limited. Deformation under large force may cause early failure. Therefore,
shape memory material is defined by two criteria, one is the ability to undergo shape deformation, and the second is the amount of energy that can be stored and recovered. These can be predicted from the DMA length peak based on the maximum strain and maximum static force. Considering the thermal expansion introduced as temperature increase, the degree of length recovery is semi-quantitative.

4.4 Conclusions

During damage-repair cycle, spatial and temporal synchronization of physical remodeling and chemical reactions are essential to recover mechanical properties. This chapter shows that for MGP-PUR-Zn(OAc)$_2$ networks, besides H-bond and covalent bond formations that re-bond the cleaved chain ends, the physical driving force for damage closure and generation of interfacial contacts is the shape memory effect attributed to stored entropic energy. While majority of the previous studies utilizing chain diffusion of melted polymers to induce repair, using the concept of shape memory initiated self-repair, self-healing polymer matrices can be selected based on their shape memory properties within the desired temperature range. Because shape recovery occurs within the glass transition or rubbery region, self-healing occurs without melting or reshaping the material.

To select the polymer matrix for shape memory driven self-repair, assessment of shape memory properties is required. However, there is no efficient or standard method of charactering it. Generally used method is shown in Figure 5.3, but the process of obtaining desired strain without sample rupture is tedious. The resulting shape recovery ratio R is highly depend on experimental conditions that comparison between different
materials and different runs are of no physical meaning. This chapter illustrates a new approach to predict the SME for polymers. A length change peak is observed in an DMA experiment for MGP-PUR-Zn(OAc)₂ network, which is shown to be manifested by materials viscoelastic properties. Therefore, this behavior can be utilized to predict the polymers SME from the perspectives of deformability and recoverability, as well as the onset temperature for SME.

Future work will be focusing on several aspects pertaining to the physics of self-healing and prediction of SME. The shape recovery process during damage-repair cycle MGP-PUR-Zn(OAc)₂ will be analyzed using computer modeling. Spatial distribution of the internal stress generated as a result of mechanical damage as well as release of the stress as a function of time will be calculated. More work will be focused on analyzing the DMA length peak of different polymers with different molecular weight and crosslink density, and correlate it with their shape memory properties. The relations between the length peak and material properties including crosslink density, tan δ, E’, E”, and Tg should be established. Since the stored energy (E) at the length peak can be calculated from the stress (σ) and strain (ε) at maximum length \(E=0.5 \sigma \times \varepsilon\). Then a 3-D plot of E as a function of crosslink density and tan δ can be generated, and utilized for prediction of shape memory property of any polymers based on these parameters from a single experiment.
CHAPTER 5  THERMODYNAMICS OF SELF-HEALING

5.1 Introduction

Three fundamental questions pertaining to self-healing of polymer materials are (1) what are the networks physical properties that enable certain chemical reactions to facilitate self-healing and others do not, (2) what chemical reactions offer self-healing attributes for a given polymer physical environment, and (3) how re-bonding of cleaved or dislocated macromolecular segments lead to physical reconstruction of a wound. Although the last decade has offered a number of new discoveries that significantly enhanced our limited understanding in self-healing materials,[158-161] there are still many unanswered questions. Although from the chemical point of view, just like any other chemical process, self-healing will be governed by thermodynamics and/or reaction kinetics, how chemical reactions can be synchronized with physical network remodeling is intriguing. Although classification of these complex processes into intrinsic or extrinsic (with or without add on components) was suggested, polymers will not repair by themselves unless their intrinsic properties, such as chemical or physical compositions are altered. Whether self-healing components are chemically attached to a polymer backbone or physically dispersed in a polymer matrix, these intrinsic properties (physical/chemical compositions and concentrations, density, elasticity, specific energy) will determine the ability to repair. One could perhaps argue that thin polymer films may exhibit different self-healing properties compared to their bulk counterparts, thus classifying it as extrinsic process, these attributes are driven by physico-chemical processes characteristic of a given intrinsically driven self-healing process.
Traditionally, damaged materials are mainly repaired by welding, gluing, or patching. The concept of self-healing is to enable a material to repair damages with a minimum intervention. From the thermodynamics point of view, in order for a chemical process to proceed spontaneously, the total energy of the process, \( \Delta G (=\Delta H - T\Delta S) < 0 \). As was pointed above, during damage of macromolecular networks, the two main events are chain cleavage and/or chain slippage. While the former generates reactive groups, the latter may lead to conformational changes. If re-mending of ruptured networks ought to occur autonomously, the interplay of healing reactions and chain rearrangements is critical.

While the majority of recent developments in self-healing focused on synthetic aspects, it is noteworthy that physical aspects of self-healing are rarely considered. But this does not diminish the role of physical network properties in designing networks, which are as important as chemical reactions. Initial studies on thermoplastic polymers suggested that self-healing of a crack involves five stages: segmental surface rearrangements, surface approach, wetting, diffusion, and randomization.\[^6\] In essence, the outcome of this process was to regain mechanical properties at the repaired area via chain entanglements. Thus, chain diffusion at the polymer-polymer interface was considered the primary driving force for repairs, and the reptation model[140, 141] semi-quantified these events by describing the motion of macromolecular segments trapped in a stationary tube[142]. Self-healing was achieved only when the entire chain completely disengaged from the tube, reaching equilibrium state after a given time \( T_r \) (\( T_r \) is the time required for complete chain disengagement from the tube). Using this concept, self-
repairing process can be viewed as chain conformational changes going from non-Gaussian to equilibrated Gaussian state during which each chain escapes from the tube cavity in a given time. As expected, longer chains would take longer to escape, and this approach provided the molecular weight (M) dependence of repair time \( T_r \propto M^3 \), implying that lower molecular weight polymers exhibit favorable repairing conditions. Assuming no bond cleavage during damage, chain diffusion was the only driving force for repair, and the source of loose chain ends was chain slippage. In this context, healing efficiency \( R(\sigma) \) can be defined by the extent of the recovery with respect to its initial post-damage state as the ratio of fracture stress before (\( \sigma_{\text{initial}} \)) and after healing (\( \sigma_{\text{healed}} \)):  

\[
R(\sigma) = \frac{\sigma_{\text{healed}}}{\sigma_{\text{initial}}} \tag{1}
\]

Previous studies have also shown that the fracture stress is related to \( M \) and \( t \) via \( \sigma \propto (t/M)^{1/4} \) (where: \( t \) is the repairing time). If during time \( t \), a chain escapes the tube at \( T_r \), and repair is completed, then \( t = T_r \). This would imply that conformation changes result in self-healing. Conceptually, if repair is considered as the rearrangement of chain conformations from non-Gaussian to Gaussian states, the time required for chain to escape the tube as well as the recovery of fracture stresses will again favor low molecular weight polymers that exhibit shorter repairing times and energetically favorable stress recoveries due to enhanced mobility. The \( \sigma \propto t^{1/4} \) dependence is well accepted and was experimentally shown for induced crack healing in poly(methyl methacrylate) (PMMA)[162, 163] as well as theoretically predicted using other theoretical approaches[164, 165].
While the reptation model offered the t and M dependence of healing efficiency R, it is limited by not considering chain cleavage as well as intermolecular interactions, which both are reflected in glass transition temperature (T_g) values and bond reforming reactions. Although maintaining temperature above the T_g (large free volume) may be a pre-requisite for self-healing, as will be seen, this condition is not a necessity.

5.2 Self-healing Recoupling Lattice Model

To examine how the thermodynamic behavior of chains at localized damaged areas favor autonomous healing, entropy and enthalpy contributions were considered.[166] Self-healing of damaged polymer networks can be viewed as a transition from non-equilibrium to equilibrium state via a series of infinitesimal equilibrated steps described via self-healing recoupling lattice model shown in Figure 5.1, A and B, where A represents the state after damage, and B represents the state after repair. The half circles (red) represent cleaved chain end (A), whereas full circles (red) are remended chain ends after reaction (B). During this process, two types of macromolecular domains are generated as a result of mechanical damage: (1) free chain ends resulting from chain rupture with both chain ends being free, and (2) tethered chain ends having one end anchored to undamaged networks and the other reactive dangling ends.

Positive entropy changes from state A to state B is anticipated due to the volume increase near created interfaces which will lead to an increase of the number of arrangements available for a given state. Driven by the positive entropy changes as well as network density gradients near damaged area, chain ends will continuously expand into open voids and thus fill the damage, particularly when two surfaces are in favorable
distances. However, unlike freely diffusing small molecules, entropy changes of polymeric chains are much smaller due to limited mobility in the surroundings of polymer matrix confinements. Therefore, flexibility of chains becomes critical.

Figure 5.1. Recoupling self-healing lattice model of reactive chain ends at damaged polymer interface. Figure A represents the damaged state, with dangling chains and voids, whereas Figure B is the repaired state during which reactive chain ends crosslink with their counterparts. Each square represents a single lattice site occupied by one segment of a polymer chain. Half-circles (Figure A) represent reactive chain ends, whereas full circles (Figure B) are re-mended chain ends. Full blue circles represent undamaged segments of the polymer lattice.

Flexibility of chains, reflected by the $T_g$ of a given polymer, will have a significant effect on number of chain configurations, thus affecting entropy changes which is mainly localized near the damaged area primarily occupied by dangling ends (half circles, Figure 5.1). For that purpose Flory’s flexibility parameter ($f$) can be adopted to describe the localized energy changes during repair.[167] As shown in Figure 5.1, n self-avoiding
walk polymer chains, each has \( N \) segments\(^1\), \((N-1)\) bonds and \((N-2)\) bond angles, can be fitted into a self-healing recoupling lattice, where each segment occupy one lattice site. \( \Delta G \) dependence as a function of chain flexibility can be obtained by considering chains being semi-flexible, and \( f \) defined as the probability of two successive bonds to be not collinear and are subject to rotations. Therefore, out of \( n(N-2) \) bonds, there will be \( fn(N-2) \) bent bonds. Under the condition that \( \partial \Delta G/\partial f = 0 \), \( f \) can be described as

\[
f = \frac{(z-2)e^{-\varepsilon/k_BT}}{1+(z-2)e^{-\varepsilon/k_BT}}
\]

where: \( z \) is the coordination number of the lattice unit, \( k_B \) is Boltzmann constant, \( T \) is the absolute temperature, and \( \varepsilon \) is the energy difference between collinear and bent bonds. Assuming that the energy of inter-macromolecular interactions is zero, \( \Delta G \) for free chains with two ends free will be given as

\[
\Delta G = -T\Delta S = -nRT\{\ln N + \ln(z/2e) + (N-2)\ln[1/(1-f)e]\}
\]

The above approach was employed to calculate the energy changes of free dangling chain ends in the self-healing lattice, where \( \ln N \) is the probability of finding one end of each chain in a random location. However, for tethered chains (one end is anchored and the other end is free to move), \( \ln N = 0 \). Thus, \( \Delta G \) of tethered chain ends can be expressed as

\[
\Delta G = -T\Delta S = -nRT\{\ln(z/2e) + (N-2)\ln[1/(1-f)e]\}
\]

In this approach, it is critical that a threshold value for \( f \) is given as \( K \), where when \( f = K \), \( \Delta G = 0 \). According to Eqns. (3) and (4), when \( f > K \), \( \Delta G < 0 \) and the chains will be able

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\(^1\) Segment is defined as a repeating unit or a macromolecular unit that maintains its conformation during repair.
to move spontaneously. When \( f < K \), the chains will be too rigid to undergo conformational changes, making repair unlikely to occur, or requiring higher external energy inputs to overcome thermodynamic or kinetic barriers. It can be shown that for free chains \( K \) is

\[
K_F = 1 - \left( \frac{1}{e} \right) \left( \frac{zN}{2e} \right)^{1/N-2}
\]  

(5)

whereas for tethered chains, \( K \) becomes

\[
K_T = 1 - \left( \frac{1}{e} \right) \left( \frac{z}{2e} \right)^{1/N-2}
\]  

(6)

For example, for tethered chains with the coordination number \( z = 6 \) that consist of 20 segments, \( K_T = 0.63 \), and \( f \) need to be >0.63 for self-healing to occur. For a free chain with 20 segments, however, \( K_F = 0.56 \), suggesting that the requirement for chain flexibility is lower to initiate conformational changes. Since the \( K \) value increases with the increasing number of chain segments, therefore, longer chains will require higher flexibility to acquire conformational changes. The primary consequence of mechanical perturbations of the lattice will be lowering molecular weight to favors chain mobility and repair.

The above approach provided a fairly good estimate of self-healing capabilities by correlating the chain length, the energy difference between chemically dependent collinear and bent bonds (\( \varepsilon \)), and the entropy of chain rearrangements. As was shown, tethered and free chains exhibit higher mobility compared to undamaged chains, but free chains have higher \( f \) values due to lower \( \varepsilon \), and typically smaller \( N \), compared to tethered chain population. The net result: more negative \( \Delta G \) of the network, greater chain mobility. This concept can be validated by considering polyurethane crosslinked network
which cannot self-heal by itself, but when stable dangling chains along crosslinked backbone are generated due to damage, self-repair will occur.[168]

The above predictions lead to further insights of self-healing; specifically, how tethered/free chains contribute to damage-repair cycle. Using Eqns. (3) and (4), Figure 5.2 was constructed to illustrate the relationship between the free energy changes $\Delta G$ (assuming $\Delta G = -T\Delta S$) of free (surface A) and tethered chain ends (surface B), the number of chain segments $N$, and chain flexibility $f$. As shown in Figure 3, $\Delta G=0$ plane represents polymer chains at equilibrium. Above the plane ($\Delta G<0$), spontaneous repairs will occur, whereas below ($\Delta G>0$), self-healing will be inhibited. The two red points represent the critical $f$ values for free ($K_F$) and tethered ($K_T$) chain ends when $N = 20$, whereas the solid red curve illustrates how $\Delta G$ changes are affected by the increasing $N$ (higher molecular weight). During healing, both free and tethered chain ends react with each other, contributing to the increase of $N$. As $N$ increases, the energy required for chains to bend also increases, chains become more rigid, and $\varepsilon$ increases, leading to the decrease of $f$ (Eqn. (2), until it reaches the threshold value of $K$ for a given $N$ and $\Delta G = 0$. At this point, a stable Gaussian equilibrium state is reached and when $f < K$ after damage, which falls in the area below $\Delta G=0$, repair will be inhibited.

According to Eqn. (3) and (4), low molecular weight (low $\varepsilon$, high $f$) polymers will favorably contribute to $\Delta S$ values, thus making $\Delta G < 0$. Enthalpy changes ($\Delta H$) during damage-repair cycles will also impact $\Delta G$, and in order for self-healing to be spontaneous under given conditions, $\Delta H < 0$. Upon damage, internal energy ($E_{int}$) will increase due to work ($W$) and heat ($Q$) transfer, thus $\Delta H$ requirement will be met. At the same time, upon
mechanical damage, the system will become metastable. Under these conditions, reactive ends may be intercepted by other undesirable reactants, thus resulting in non-repairable damage. The presence of stable reactive ends will favor self-healing, which upon rebonding will form a new equilibrium state enhanced by external energy (E_{ext}) input or favorable kinetic and thermodynamic network conditions when \( \Delta H < 0 \). This can be also accomplished by incorporating specific bonds, typically weaker than the surroundings, which upon cleavage reassemble. Perhaps the most illustrative examples are H-bonding, stable free radicals, or coordination bonds. Another approach is incorporation of stimuli-responsive components into a polymer backbone.

Heat or electromagnetic radiation are the most often used sources of stimuli. As a result of absorption, potential and kinetic energy of chains and chain ends will increase, thus creating thermodynamically and kinetically favorable recoupling \( \Delta H \) and \( \Delta S \) conditions. For higher initial N value chains (higher molecular weight), shorter segments formed during damage will further enhance chain flexibility \( f \), thus favoring repairs. Also, incorporation of stimuli-responsive reactive groups will offer enthalpically and entropically favorable conditions enabling the repairing of rigid networks. This can be envisioned in Figure 5.2 by bringing both surfaces A and B from \( \Delta G > 0 \) into \( \Delta G < 0 \) space, enabling even non-flexible polymer segments to repair. Although heat and electromagnetic radiation are the most common energy (E_{ext}) sources utilized to initiate self-healing reactions, it is often difficult to differentiate which portion of the electromagnetic radiation directly causes self-healing and which results in local
temperature changes, potentially resulting in the same net effect – network repair. Thus, utilizing discrete sources of energy with minimal intervention is particularly appealing.

**Figure 5.2.** Gibbs free energy changes ($\Delta G = -T\Delta S$) plotted as a function of number of segments ($N$) in a polymer chain and flexibility parameter ($f$) for free (surface A) and tethered chain ends (surface B). The $\Delta G=0$ kJ/mol plane represents polymer chains at equilibrium. Above the $\Delta G=0$ plane ($\Delta G<0$), spontaneous repairs occur, whereas below the $\Delta G$ plane ($\Delta G>0$), self-healing will not take place. Two red cross represent the critical $f$ values for free ($K_F$) and tethered ($K_T$) chain ends for $N = 20$. The solid red curve illustrates how $\Delta G$ changes are effected by increasing $N$ values (high molecular weight).

5.3 Conclusions

Inspired by Nature, self-healing materials represent the forefront of recent developments in materials chemistry and engineering. Although from the chemical point
of view, just like any other chemical process, self-healing will be governed by thermodynamics and/or reaction kinetics, how chemical reactions can be synchronized with physical network remodeling is critical. In this chapter, a self-healing lattice model is developed to describe the thermodynamic requirements for self-healing networks in the context of conformation changes that contribute to the Gibbs free energy. It is demonstrated that chain flexibility significantly contributes to the entropy changes, whereas the heat of reaction and the external energy input are the main contributors to enthalpy changes. It should be noted that this model describes only how thermodynamics of the tangling and free chains localized within the damaged interface contribute to self-healing, which has been largely neglected in previous research. Future study may focus on experimentally measurements and computer simulations to describe these events. Besides interfacial diffusion, how elasticity of materials surrounding the damaged areas facilitates self-healing will be discussed in Chapter 5 of this thesis.
CHAPTER 6  ENCODING COLOR, SHAPE MEMORY, AND SELF-HEALING IN HETEROGENEOUS POLYURETHANES

6.1 Introduction

Although recent studies focused on mechanochromic molecules imbedded into polymer matrices,[169, 170] encoding shape changes and self-healing attributes with color responsiveness brings materials one step closer to nature. Since each of these attributes requires volume changes at different length scales, built-in heterogeneity appears to be one of the prerequisites in designing new generations of materials. For example, color changes typically require molecular trans-cis conformational changes[171, 172] or ring opening reactions[173, 174], whereas the shape changes are usually achieved by shape memory effect (SME) that occur at nano- and macro-scales driven by viscoelastic properties[145, 153, 175, 176]. Self-healing, on the other hand, may involve bond reformations as well as macromolecular rearrangements at all scale lengths.[177] Thus, bringing these attributes into one material requires interplay between molecular macroscopic events and heterogeneities.

This study reports the development of heterogeneous polymers that exhibit phase separated morphologies achieved by a chemical makeup and directional drawing that lead to fibrous morphologies of polycaprolactone (PCL) and polyurethane (PUR) phases. Figure 6.1 illustrates the chemical makeup of the system which consists of spiropyran (SP) that serves as a mechanochromic sensor, 1,4-butanediol (1,4-BD), polycaprolactone (PCL-diol), and hexamethylene diisocyanate (HDI), that facilitate shape memory and
self-healing properties, and dibutyltin dilaurate (DBTDL) as the catalyst. A prepolymer method was utilized to reacy SP and PCL-diol with HDI, resulting in OH terminated prepolymer. Upon further reactions with 1,4-BD and HDI, SP functionalized polyurethane (PUR-PCL-SP) was formed. Details regarding the polymer synthesis are described in the Experimental Section.

![Chemical structure](image)

**Figure 6.1.** A - Synthesis of SP-PUR fibers containing spiropyran (SP), 1,4-butanediol (BD), polycaprolactone (PCL), and hexamethylene diisocyanate (HDI) in the presence of dibutyltin dilaurate (DBTDL).

6.2 Experimental Methods

Hexamethylene diisocyanate (HDI), 1,4-butanediol (1,4-BD), dibutyltin dilaurate (DBTDL) were purchased through Sigma-Aldrich. Polycaprolactone diol (PCL) of molecular weight ~4000 was provided by Daicel Corp. Tetrahydrofuran (THF) was purchased from Fisher Scientific and dried using 3A molecular sieves before use.
Spiropyran molecules were provided by Dmitriy Davydovich and synthesized according to previously published methods.[178-181]

Prepolymers terminated with OH groups were obtained by first reacting SP (8 mg) in molar excess of HDI (8 μL) in THF (1.5 ml) at 50°C for 5 mins catalyzed by DBTDL (2 μL). The solution was then added into melted PCL (1.25 g) and reacted at 70°C for 10 mins. Then additional HDI (51 μL) was added and reacted for another 30 mins, forming solution A containing the prepolymer dissolved in THF. To make SP-PUR-P fiber, 1,4-BD (0.058 g) and HDI (113 μL) was dissolved in THF (0.4 ml) and added into solution A. Upon complete mixing, SP-PUR-P fibers were drawn from the solution at room temperature. After drying at RT for 30 mins, the fibers were further cured at 50°C for overnight. SP-PUR-M fibers were produced by adding the same amount of 1,4-BD and HDI into pre-polymer solution A, and then dried at RT for 30 mins after sufficient mixing, followed by curing at 50°C for overnight. The resulting polymer was then melted at 160 °C and fibers are drawn from the melt.

Tensile stretch test was carried out on Instron 4502 at room temperature (21 °C) at a rate of 48 mm/min. The testing area was 10 mm. Data was collected by averaging the results from 6 specimens.

Dynamic mechanical analysis (DMA) were performed on a TA Instrument Q800 DMA. Dynamic mechanical properties were measured from -100°C up to 100°C while
heating at 2°C/min. Dynamic moduli and mechanical damping (tan δ) were analyzed using TA Universal Analysis 2000.

Shape fixity ($R_f$) and shape recovery ratios ($R_r$) defined by the equations 

\[ R_f = \frac{\varepsilon_f}{\varepsilon_{max}} \times 100\% \] 

and 

\[ R_r = \frac{(\varepsilon_f - \varepsilon_r)}{\varepsilon_f} \times 100\% , \] 

whereas $\varepsilon_{max}$ is the maximum strain upon deformation, $\varepsilon_f$ is strain after load removal, and $\varepsilon_r$ is the final strain after shape recovery.

Differential scanning calorimetry (DSC) was collected using TA Instruments DSC Q-100. The calibration was carried out using indium and sapphire standards. Heating and cooling rates of 10 °C/min were used over the studied temperature range.

6.3 Results and Discussion

The deliberate choice of these components was driven by our desire to encode color, SME, and self-healing properties into one material. Using well-established reaction-spinning process [182] we produced fibrous morphologies, which were drawn from solution during the polymerization of OH terminated prepolymer with 1,4-BD and HDI. The resulting PUR-PCL-SP show two melting transition temperatures ($T_m$) at 54 and 169°C measured by differential scanning calorimetry (DSC) (Figure D-1 of Appendix D), indicating the formation of phase-separated morphologies. We examined the phase separation of fibers’ cross-sections using internal reflection IR imaging (IRIRI) with a spatial resolution of ~1 μm². This is illustrated in Figure 6.2, where graph A represents a PUR-PCL-SP fiber sliced into four 100 μm thick cross-sections ①, ②, ③,
and ④. The IR images of the cross-section of each sections are illustrated in Figure 6.2, B, where B₁-B₄ and B₁’-B₄’ show spatial distributions of the 1685 and 1724 cm⁻¹ bands, respectively. These bands correspond to the C=O vibrations of the urethane groups and PCL ester bonds, respectively. Figure 6.2, B₁-B₄ show red (high) and blue (low) domains corresponding to polyurethane (PUR) rich and poor regions. Furthermore, Figure 6.2, B₁’-B₄’ illustrates that PUR-rich areas are low in PCL (blue), but PUR-poor areas exhibit the high content of PCL (red). This is manifested by low and high intensities of PCL ether C=O vibrations. Notably, the phase separation occurs along the draw direction across ①, ②, ③, and ④ sections, but not at the surface. The IR spectra collected from PUR-rich and PCL-rich phases shown in Figure 6.2, B₁” provide further compositional information of each phase. While the Supporting Documents provide detailed analysis, the 1800-1600 cm⁻¹ carbonyl region shows that the PUR-rich domains contain PCL, but have significantly greater amounts of urethane and 1,4-BD. At the same time, the PCL rich domains contain minute quantities of urethane linkages.
Figure 6.2. A – Schematic representation of the cross-section of a 200 μm thick fiber; B - IR images of the 1685 cm\(^{-1}\) (B\(_1\)-B\(_4\)) and 1724 cm\(^{-1}\) (B\(_1\)'-B\(_4\)') bands due to PUR and PCL C=O vibrations, respectively, collected from the cross-section ①, ②, ③, and ④ marked as the squares in A for SP-PUR-P fiber; B\(_1\)” – corresponding IR spectra recorded from PUR (blue in Figure B\(_1\)'-B\(_4\)’) and PCL rich (red in Figure B\(_1\)'-B\(_4\)’) areas indicated by the arrows; C – IR images of the 1724 cm\(^{-1}\) band enlarged on a PUR rich domain (marked by the square in Figure 4, B\(_1\)’); C\(_1\) and C\(_2\) – IR spectra of carbonyl and amide II vibrational regions, where Trace 1-6 were collected from the corresponding areas shown in Figure C marked by square 1 through 6, respectively; C\(_3\) – percentage of the 1724 cm\(^{-1}\) (ester C=O) and 1685 cm\(^{-1}\) (urethane C=O) bands within 1780-1640 cm\(^{-1}\) region plotted as a function of the distance from the center of PUR domain shown in Figure C (0-9 μm). The percentage is calculated based on integrated areas of the de-convoluted bands.

Another intriguing feature of these materials is the interphase between PUR and PCL rich phases. The analysis of amide II vibrational region at 1600 - 1500 cm\(^{-1}\) as shown in Figure 6.2, B\(_1\)” indicates formation of different types of H-bonding within the two phases: 1) between NH and C=O groups of two urethane groups within the PUR rich domains (urethane-urethane, 1535 cm\(^{-1}\)), and 2) between urethane NH and ester C=O groups in the PCL rich regions (urethane-PCL, 1530 cm\(^{-1}\)).[183] Figure 6.2, C shows the IR image of the 1724 cm\(^{-1}\) band zoomed on a PUR rich domain as shown image B1’ (square), which clearly show the distinguishable PCL- and PUR-rich domains. Furthermore, the IR spectra collected from 1 though 6 of Figure 6.2, C, with 1 μm interval, are shown in Figure 6.2, C\(_1\) and C\(_2\). From the center of PUR-rich domain to
PCL-rich domain (1 through 6), the interphase is manifested by a gradual decrease of urethanes (1685 cm\(^{-1}\)) compared to PCL ester groups (1724 cm\(^{-1}\)), as well as an increase of the degree of crystallinity for PCL (narrowing of 1724 cm\(^{-1}\) band), which are shown in Figure 6.2, C\(_1\). Meanwhile, the H-bonding shifted from urethane-urethane to urethane-PCL as indicated by shifts of the amide II vibrations from 1535 to 1530 cm\(^{-1}\) (Figure 6.2, C\(_2\)). The compositional change at the interphase is further demonstrated by Figure 6.2, C\(_3\), where the percentage of urethane C=O vibrations over the total C=O vibrations are plotted as a function of the corresponding distance from the center of the PUR rich domains. The percentage of ester C=O vibrations is also plotted. As shown, from the center to the matrix, PCL increases while PUR decreases. It should be noted that pure aggregation of 1,4-BD based PUR without any PCL was not observed on this length scale. In contrast, when PUR-PCL-SP was allowed to fully polymerize before processing (melt-drawing), the phase separation and the size of the interphase are significantly smaller and non-distinguishable in IR imaging (Figure D-1, B of the Appendix D and Figure 6.3).
Figure 6.3. A - IR images of the 1685 cm$^{-1}$ ($A_1$) and 1724 cm$^{-1}$ ($A_2$) bands collected from the cross-section of a melt-drawn PUR-PCL-SP; B - corresponding IR spectra recorded from $A_2$.

The unique feature of the phase-separated PUR-PCL-SP is the ability to change color, shape memory, and self-heal. These are illustrated in Figures 6.4 and 6.5. As shown in Figure 6.4, A, when PUR-PCL-SP was elongated, its color changed from light pink (a) to bright purple (b), and the deformation can be recovered when heated to 65 °C, whereas the color change is reversible upon exposure to visible light (c). The color changes are due to the presence of SP molecules covalently incorporated into a polymer backbone. It is well established that when chains are stretched, SP rings open up, thus transforming the colorless SP into color emitting merocyanin (MC). Upon chain
relaxation due to built-in SME, MC molecules absorb the visible portion of the electromagnetic radiation and return back to the colorless SP form. When the same polymer remains in the stretched state, it takes significantly longer times (~26 hrs) for MC to return to its thermodynamically stable SP form.

The classical dual-shape memory thermomechanical cycle performed on PUR-PCL-SP fiber is shown in Figure 6.4, B with deformation temperature at 65°C and shape fixation temperature at -20°C. To induce shape recovery, the temperature was raised to 65°C, which is above the $T_m$ of PCL segments. The shape fixing ratio ($R_f$) at 20°C was 98.4% and the shape recovery ratio ($R_r$) was 96.4%. These composite materials also exhibit 3D SME. As shown in Figure 6.4, C, PUR-PCL-SP polymers were shaped into a “spider-like” structure, and the “legs” of the “spider” were stretched and flattened at 65°C, followed by shape fixation at room temperature. The recovery takes ~70 s at 65°C. At the same time, as shown in Figure 6.4, C, the color changes are the same as observed in Figure 6.4, A.
Figure 6.4. A – Shape memory cycle for SP-PUR-P fiber: (a) before deformation, (b) stretched by 800% at room temperature followed by load removal, (c) heating at 65 °C for 10 mins, then cooled to room temperature and exposed to white light for 10mins. B – Standard dual-shape memory thermomechanical cycle for SP-PUR-P with deformation temperature ($T_d$) at 65 °C, shape fixation temperature ($T_f$) at -20 °C, and shape recovery temperature ($T_r$) at 65 °C. Static force, temperature, and length are plotted as a function of time. C – Shape memory cycle for SP-PUR bulk polymer. The original shape was deformed at 65 °C followed by shape fixed at room temperature. Upon heating the temperature up to 65 °C again, the original shape was recovered in 70 s. The color disappeared by 3 hours’ exposure under visible light.
The third encoded feature in these phase-separated polymers is their ability to self-repair. As shown in Figure 6.5, A, when a 10×50 μm scratch (width×depth) was made on PUR-PCL-SP, self-healing occurred upon heating at 65°C for 10 mins, leaving a scar on the surface. To quantify the self-healing efficiency, tensile tests were performed on fibers before damage, after damage, and after repairing at several different time intervals. The values of the ultimate strain and tenacity at break are plotted as a function of time in Figure 6.5, A’. At t=0 min, damage was generated, and self-healing occurred during the course of 120 mins. These data show that after 30 mins, 91% and 68% of the original ultimate strain and tenacity were recovered, and they reached 92% and 93% after 120 mins of healing. In summary, these concentrically phase-separated materials exhibit color change, shape memory, and self-healing properties.

To identify molecular events responsible for PUR-PCL-SP self-healing, we followed chemical changes in the repaired areas using IRIRI. Figure 6.6, A illustrate optical images after repair at 65°C for 120 mins. Figure 6.6, B₁ and B₂ show the corresponding IRIRI images collected from 30×30 μm² area of the 1724 (B₁) and 1685 (B₂) cm⁻¹ bands. The corresponding spectra recorded inside (a) and outside (b) repaired areas are shown in Figure 6.6, C. Traces a and b are normalized at 1469 cm⁻¹. These data show that the repaired area exhibit higher concentration levels of PCL (1724 cm⁻¹) and lower concentrations of PUR (1685 cm⁻¹). These compositional changes were not detectable up to 60 mins of healing. These results indicate the occurrence of rearrangements and diffusion of the melted PCL chains at the damaged interface at temperatures above its T_m, which contribute to the self-healing.
Figure 6.5. A – Optical images of self-healing for PUR-PCL-SP; A’ - Tenacity at break and ultimate strain plotted as a function of self-healing time for PUR-PCL-SP; B – Optical images of self-healing for PUR-PCL-SP-M; and B’ - Tenacity at break and ultimate strain plotted as a function of self-healing time for PUR-PCL-SP-M fibers. Self-healing was performed at 65°C. The last data points in Figure A’ and B’ correspond to undamaged fibers.
Figure 6.6. A – Optical image of a cut after healing at 65°C for 120 min; B – IR images of the 1724 cm⁻¹ (B₁) and 1685 cm⁻¹ (B₂) bands collected from the square area marked in Figure A; C – IR spectra a and b collected from the repaired and undamaged areas marked in Figure B₁.

To examine whether processing conditions affect properties, melt spun PUR-PCL-SP fibers were also produced as stated earlier using the same chemical composition. This was achieved by polymerizing the prepolymer with 1,4-BD and HDI prior to fiber drawing. Shape memory analysis for melt-drawn PUR-PCL-SP are shown in Figure D-2 of Appendix D. A comparison of Rₐ and Rᵣ for the two types of fibers are listed in Table D-1 of Appendix D. IR images shown in Figure 6.3 demonstrates that the melt-drawn PUR-PCL-SP do not exhibit micron-scale phase-separated morphology at the cross-section, and their shape recovery efficiencies are also lower. Figure 6.5, B, which shows
the self-healing of melt-drawn PUR-PCL-SP, indicates significantly slower self-healing rates (10 mins at 65 °C). The recovery only reached 44% of the original strain and 49% of the original tenacity after 120 mins (Figure 6.5, B’). Considering melt processing is the only difference of chemically identical specimens, phase separation plays an important role in achieving desirable properties. Since the phase-separated SP-PCL-SP fiber exhibits enhanced SME and self-healing properties, while diffusion and rearrangements of the melted PCL segments at the damaged interface occurs at the later stage of self-healing as shown in Figure 6.6, the following mechanism of recovery from mechanical damages proposed.

Recovery of mechanical strength upon healing results from reformation of PCL crystalline phase upon heating and cooling.[152] With a melting temperature of 52 °C, when heated to 65 °C, dissociation of PCL crystalline phase initiates shape recovery from damaged or deformed state, generating interfacial contacts. Upon subsequent cooling, the crystalline phase is reformed at the interface, binding the separated chains together. The question is why the reaction-drawn PUR-PCL-SP with phase-separated morphology exhibit higher healing efficiency compared to the melt-drawn one? To address this, we further examined the SMEs of both polymeric fibers. The fibers were first stretched to 800% at RT, and upon load removal, were heated to 65 °C for 10 min to recover. This shape memory cycle mimics the temperature conditions for damage-repair cycle. The cycle was repeated four times, and for each cycle, tensile properties were measured after recovery. These results are plotted in Figure D-3 of Appendix D. Stress-strain curves remained consistent after four cycles for reaction-drawn PUR-PCL-SP, whereas for metl-
drawn PUR-PCL-SP, cycles 3-4 exhibited large deviations from the first two cycles. The $R_f$ and $R_r$ were calculated for each shape memory cycle and summarized in Table D-2 of Appendix D. For the first shape memory cycle, shape fixity of reaction drawn PUR-PCL-SP is significantly lower than the melt-drawn, indicating higher elasticity of the former at room temperature. However, the reaction-drawn PUR-PCL-SP exhibited better shape recovery manifested by a smaller remaining strain and higher $R_r$. Over the four cycles, it exhibited better shape recovery, and $R_f$ and $R_r$ values showed smaller deviations compared to melt-drawn PUR-PCL-SP. These results indicate that the phase-separated fibers are more structurally stable toward mechanical deformation compared to the one without micron-scale phase-separation.

The above data demonstrates that the phase-separated PUR-PCL-SP polymers exhibit significantly better shape recovery properties compared to the chemically identical counterparts without micron-scale phase-separation. As was proposed, self-healing is not only due to recrystallization of PCL segments, but also requires formation of contacts between the damaged surfaces driven by the SME. These results support the hypothesis as the polymer with improved SME also exhibits higher self-healing efficiency, whereas micron-scale phase-separated morphology is the main contributing factor to the enhanced SME as well as self-healing. As viscoelastic behavior is responsible for the SME and chain diffusions, in order to find out the contributing factor for the enhanced SME and self-healing, viscoelastic properties were examined using dynamic mechanical analysis (DMA). The DMA curves are shown in Figure D-4 of the Appendix. The storage modulus ($E'$), loss modulus ($E''$), and tan δ values at 20 °C and 65
°C are listed in Table 6.1. Reaction drawn PUR-PCL-SP has lower E’ and E”, while its tan δ is lower at 20 °C but higher at 65 °C. Viscoelastic characteristics are related to the formation of phase-separated morphology. Since E’ and E” of the reaction-drawn PUR-PCL-SP became significantly lower at 65 °C above the T_m of PCL-rich phase, chains exhibit higher mobility. Therefore, following the generation of interfacial contacts facilitated by SME, rearrangements and diffusion of the melted PCL chains at the damaged interface took place, which contribute to the enhanced self-healing.

Viscoelastic characteristics of SP-PUR-P are related to the formation of phase-separated morphology. When HDI molecules are reacted with 1,4-BD and OH terminated PCL during fiber drawing, after fiber formation, THF quickly evaporates, and PCL prepolymer chains crystallize. It is speculated that during this process, HDI and 1,4-BD monomers are expelled into the amorphous regions where there is more free volume, forming PUR rich domains. Furthermore, since the resulting 1,4-BD polyurethane segments form strong urethane-urethane H-bonds, thus exhibit low solubility in THF as well as low miscibility with PCL segments,[139] therefore forming a large interphase with gradual composition change. The lower moduli of SP-PUR-P above T_m demonstrate that, since PCL chains within the matrix are crystalized prior to the formation of PUR rich domains, there are less entanglements between these chains. However, when fibers are drawn from melt (SP-PUR-M), the polymers are heated at 160 °C to dissociate all H-bonds, the chains rearrange to adopt the most thermodynamically favorable state, the interphase disappears, and more entanglements are formed.
Based on these results, the mechanism for self-healing is proposed. First, after mechanical damage, the built-in SME enables shape recovery, facilitating damage closure and generating interfacial contact between damaged surfaces. Within the interface, the melted PCL chains have sufficient mobility to diffuse and rearrange. Upon subsequent cooling, recrystallization of PCL chains leads to recovery of mechanical strength. Combination of the extent of shape recovery, the rate of chain diffusion, and the degree of crystallinity, determine the final self-healing property, and efficiency of each these step is affected by the fiber’s phase morphologies.

Table 6.1. Storage modulus (E’), loss modulus (E’”), and tan δ values at 20 °C and 65 °C for reaction-drawn and melt-drawn PUR-PCL-SP.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>20 °C</th>
<th>65 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>E’ (N/tex) E” (N/tex) tan delta</td>
<td>E’ (N/tex) E” (N/tex) tan delta</td>
</tr>
<tr>
<td>Reaction-drawn PUR-PCL-SP</td>
<td>0.233 0.0153 0.0659</td>
<td>0.00217 0.00053 0.241</td>
</tr>
<tr>
<td>Melt-drawn PUR-PCL-SP</td>
<td>0.3934 0.0279 0.0716</td>
<td>0.0148 0.00265 0.180</td>
</tr>
</tbody>
</table>

6.4 Conclusions

In summary, we developed a multi-functional polymeric fiber encoded with color change, shape memory, and self-healing attributes in one. The fiber exhibit unique phase separated morphologies achieved by a chemical makeup and directional drawing that lead to fibrous morphologies of polycaprolactone and polyurethane. While melting and recrystallization of the PCL are responsible for binding the separated chains together to
self-heal, self-healing is achieved in a three-step process: 1) SME facilitated interfacial contact between damaged surfaces, 2) chain diffusion and rearrangements at within the interface, and 3) recrystallization of PCL chains upon cooling, leading to recovery of mechanical strength. The built-in heterogeneity and interphase structure are critical in achieving enhanced shape memory and chain diffusivity at the interface, thus lead to self-healing attributes.
CHAPTER 7 CONCLUSIONS AND FUTURE OUTLOOK

Synthetic materials capable of respond to external or internal stimuli represent one of the most exciting and emerging areas of scientific interest and unexplored commercial applications. Material that can respond the mechanical damages and repair themselves via chemical and physical remodeling is one of the advances. While individual structural components of polymeric networks are responsible for localized chain responsiveness, desirable spatial and energetic network properties are necessary for collective and orchestrated responsiveness to external or internal stimuli. The main challenge is to design self-healing polymeric materials that exhibit high $T_g$ and offer remote self-healing trigged by electromagnetic radiation, electric and/or magnetic fields, and environmental or atmospheric changes. While there are many exciting challenges facing this field, there are a number of opportunities in design, synthesis, and engineering of self-repairable polymeric systems and Mother Nature serves as a supplier of endless inspirations.

The study presented in this dissertation is inspired by the role of carbohydrates in biological systems as energy storage molecules and structural components. The multiple OH groups and conformation of the pyranoside ring offer unique reactivity and H-bonding abilities relating to structural and recognition properties. However, their roles in many biological processes are still unknown. This study incorporated methyl α-D-glucopyranoside (MGP), which is a methylated carbohydrate molecule, into crosslinked polyurethane networks by reacting their OH groups with isocyanates. When network formation is catalyzed by organotin based catalyst, it is capable of self-repair under
atmospheric conditions at ambient temperatures. Self-healing is due to the reaction of MGP-OH groups with atmospheric CO$_2$ and H$_2$O, thus reforming covalent linkages capable of bridging cleaved network segments. Complex formation between organotin catalyst and MGP-urethane linkages facilitated such reaction. Mechanical properties are recovered during self-repair process. These materials resemble behavior of plants during photosynthesis, but unlike plants, MGP-PUR networks require no photo-initiated reactions, thus are capable of repairs in dark in air.

However, when organotin catalyst is replaced by zinc acetate (Zn(OAc)$_2$), similar network composed MGP and PUR exhibited completely different self-healing behavior and chemical re-bonding mechanism. Self-healing proceeds at elevated temperatures. Three components are critical in the design of this system: generation of primary amines upon mechanical damage as a result of urethane bond cleavages, higher reactivity of MGP-urethane linkages, and the activity of Zn(OAc)$_2$ in catalysing urethane exchange reactions. As a result, the damage-induced amines are able to react with MGP-urethane groups catalysed by Zn(OAc)$_2$ to reform covalent linkages, thus restore mechanical properties upon mechanical damage. This process is analogous to metabolism in biological systems, where molecules used for reconstructing cell components are produced from the break down of organic matter, and amine functionalities are perhaps the most prevalent reactive groups responsible for maintaining living functions at cellular and organ levels.

Although from the chemical point of view, just like any other chemical process, self-healing will be governed by thermodynamics and/or reaction kinetics, how chemical
reactions can be synchronized with physical network remodeling is critical. A self-healing lattice model is developed to describe how thermodynamics of the tangling and free chains localized within the damaged interface contribute to self-healing, which has been largely neglected in previous research. The model is established in the context of conformational changes that contribute to the Gibbs free energy. It is demonstrated that chain flexibility significantly contributes to the entropy changes, whereas the heat of reaction and the external energy input are the main contributors to enthalpy changes. Meanwhile, macroscopically, the physical driving force for damage closure and generation of interfacial contacts is the shape memory effect attributed to stored entropic energy. This is illustrated by the MGP-PUR-Zn(OAc)$_2$ networks. While majority of the previous studies utilizing chain diffusion of melted polymers to induce repair, using the concept of shape memory initiated self-repair, self-healing polymer matrices can be selected based on their shape memory properties within the desired temperature range. Because shape recovery occurs within the glass transition or rubbery region, self-healing occurs without melting or reshaping the material.

Based on these studies, a three-step process is proposed for the self-healing polymers: 1) shape memory effect induced damage closure, which generates interfacial contacts; 2) chain rearrangements within such interface along with 3) subsequent bond reformations lead to recovery of mechanical strength. These steps are consecutive but with overlaps. To prove this concept, a multi-functional material is designed encoding shape memory and self-healing properties with color responsiveness in one. Phase separated morphologies are achieved by a chemical makeup and directional drawing that
lead to fibrous morphologies of polycaprolactone and polyurethane. While melting and recrystallization of the PCL domain is responsible for binding the separated chains together, the built-in heterogeneity and interphase structure are critical in achieving enhanced shape memory, interfacial diffusion, and lead to self-healing attributes. This study not only validates the three-step self-healing model, but also shows that molecular design and material processing together will lead to advanced material properties.

Future study may focus on experimental measurements and computer simulations to describe these events both spatially and temporally. Spatial distribution of the internal stress generated as a result of mechanical damage, and release of the stress during shape recovery as a function of time, can be simulated. Designing experiments to directly or indirectly measure the diffusion of the cleaved chains localized within the interface upon formation of interfacial contacts driven by SME would be critical. Perhaps one of the most intriguing perspectives might be developing of a general method to evaluate shape memory properties of selected polymer matrices for self-repair. This study demonstrated that the length change peak observed in a DMA experiment during glass transition, which is manifested by materials viscoelastic properties, can be utilized to indicate the SME from the perspectives of deformability and recoverability, as well as the onset temperature for SME. In future work, by analyzing the DMA length peak of different polymers with different molecular weight and crosslink density, and quantitative and qualitative correlations between the length peak and shape memory as well as self-healing properties can be established, whereas the ultimate objective is to be able to reliably predict SME of any polymers from a single experiment.
Figure A-1. Storage modulus (log $E'$ (MPa)), loss modulus (log $E''$ (MPa)), and tan $\delta$ of MGP-PUR-DBTDL (traces a, b, and c) and PUR-DBTDL (traces a', b', and c') measured as a function of temperature using dynamic mechanical analysis (DMA).
Table A-1. Relevant IR and Raman vibrational bands detected in MGP-PUR-DBTDL networks and their assignments.

<table>
<thead>
<tr>
<th>IR Wavenumber (cm⁻¹)</th>
<th>Raman Tentative Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>3346</td>
<td>st N-H + st O-H</td>
</tr>
<tr>
<td>2923</td>
<td>st C-H</td>
</tr>
<tr>
<td>2856</td>
<td>st asym C=O (free urethane)</td>
</tr>
<tr>
<td>1715(sh)</td>
<td>st asym C=O (MGP-urethane)</td>
</tr>
<tr>
<td>1696</td>
<td>st asym C=O (PEG-urethane and triisocyanate ring)</td>
</tr>
<tr>
<td>1681</td>
<td>st asym COO (DBTDL chelated)</td>
</tr>
<tr>
<td>1558</td>
<td>st C-N + δ N-H (urethane)</td>
</tr>
<tr>
<td>1535</td>
<td>δ asym C-H</td>
</tr>
<tr>
<td>1462</td>
<td>δ asym C-H</td>
</tr>
<tr>
<td>1427</td>
<td>st sym C-N</td>
</tr>
<tr>
<td>1408</td>
<td>st sym COO (DBTDL chelated)</td>
</tr>
<tr>
<td>1376</td>
<td>δ sym C-H</td>
</tr>
<tr>
<td>1350</td>
<td>δ sym CH (O-CH₂)</td>
</tr>
<tr>
<td>1335</td>
<td>δ sym C-H</td>
</tr>
<tr>
<td>1247</td>
<td>st asym N-CO-O + st (C-O-C)</td>
</tr>
<tr>
<td>1142</td>
<td>δ C-O-C (MGP)</td>
</tr>
<tr>
<td>1100</td>
<td>st C-O-C (PEG)</td>
</tr>
<tr>
<td>1083</td>
<td>st sym CO₂²⁻ (Sn-CO₂⁻)</td>
</tr>
<tr>
<td>1050</td>
<td>st sym N-CO-O + st (C-O-C) (urethane and MGP)</td>
</tr>
<tr>
<td>866</td>
<td>st asym C-N-C (tertiary amide) + st C-O-C (organic carbonate)</td>
</tr>
<tr>
<td>736</td>
<td>δ CO₂²⁻ (Sn-CO₂⁻)</td>
</tr>
<tr>
<td>683</td>
<td>Sn-O-Sn</td>
</tr>
<tr>
<td>661</td>
<td>δ sym C=O (MGP-urethane)</td>
</tr>
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</table>
Appendix B: SUPPORTING DOCUMENTS FOR CHAPTER 3

Figure B-1. Storage modulus, loss modulus, and tan delta of MGP-PUR-Zn(OAc)$_2$ (trace a, b, and c) and PUR-Zn(OAc)$_2$ (trace a’, b’, and c’) measured as a function of temperature using dynamic mechanical analysis (DMA).
Table B-1. Relevant IR and Raman vibrational bands detected in MGP-PUR-Zn(OAc)$_2$ networks and their assignments.

<table>
<thead>
<tr>
<th>Wavenumber (cm$^{-1}$)</th>
<th>IR</th>
<th>Raman</th>
<th>Intensity changes upon damage</th>
<th>Intensity changes after repair</th>
<th>Tentative Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1756</td>
<td>↓</td>
<td>-</td>
<td>-</td>
<td>↓</td>
<td>st C=O (HDI trimmer)</td>
</tr>
<tr>
<td>1710</td>
<td>↑</td>
<td>↓</td>
<td>↓</td>
<td>st C=O (free urethane)</td>
<td></td>
</tr>
<tr>
<td>1680</td>
<td>↓</td>
<td>↓</td>
<td>st C=O (MGP-urethane, PEG-urethane and triisocyanate ring)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1633</td>
<td>↑</td>
<td>-</td>
<td>st C=O (urea)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1627</td>
<td>↑</td>
<td>-</td>
<td>st N-H (R-NH$_2$)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1562</td>
<td>↑</td>
<td>-</td>
<td>δ N-H (urea)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1527</td>
<td>↓</td>
<td>↓</td>
<td>δ N-H (urethane)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1440</td>
<td>-</td>
<td>-</td>
<td>δ asymmetric C-H of hexane segments</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1328</td>
<td>↑</td>
<td>-</td>
<td>δ NC-H</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1305</td>
<td>↑</td>
<td>-</td>
<td>δ symmetric C-H of hexane segments</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1285</td>
<td>↑</td>
<td>-</td>
<td>δ OC-H</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1240</td>
<td>↑</td>
<td>-</td>
<td>st C-N (urea)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1243</td>
<td>↓</td>
<td>↓</td>
<td>st C-N (urethane)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1150</td>
<td>↓</td>
<td>-</td>
<td>st C-O-C (MGP-urethenas)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1094</td>
<td>↓</td>
<td>-</td>
<td>C-C skeletal vibrations of hexane segments</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1081</td>
<td>↑</td>
<td>↑</td>
<td>st C-OH (MGP) + δ C-O-C (urea)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1067</td>
<td>↑</td>
<td>-</td>
<td>NC-C vibration</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1045</td>
<td>↓</td>
<td>↓</td>
<td>st C-O-C (MGP-urethenes)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1036</td>
<td>↓</td>
<td>-</td>
<td>OC-C vibration</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1005</td>
<td>↑</td>
<td>-</td>
<td>st C-OH (MGP)</td>
<td></td>
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**Figure B-2.** Thermogravimetric analysis (TGA) of MGP-PUR containing 1.2\% (solid line) and 8.4\% (dash line) of Zn(OAc)$_2$. 
Appendix C: SUPPORTING DOCUMENTS FOR CHAPTER 4

Figure C-1. (A) Storage (a) and loss (b) moduli, tan delta (c), and length changes (d) of PTHF-PUR film measured as a function of temperature using dynamic mechanical analysis (DMA). (B) The time required for film to recover from the deformed curled shape to the original shape at various recovery temperatures ($T_{SR}$). Same shape recovery cycle was conducted as shown in Figure 4.4, B.
Figure C-2. Storage (a) and loss (b) moduli, tan delta (c), and length changes (d) of PCL-PUR fiber specimen measured as a function of temperature using dynamic mechanical analysis (DMA).
Appendix D: SUPPORTING DOCUMENTS FOR CHAPTER 6

Figure D-1. DSC of SP-PUR-P (A) and SP-PUR-M (B).

SP-PUR-M fibers may also have phase-separation, but with domain size below micron-scale and significantly smaller interphase.
Figure D-2. Standard dual-shape memory thermomechanical cycle and SP-PUR-M with deformation temperature ($T_d$) at 65 °C, shape fixation temperature ($T_f$) at -20 °C, and shape recovery temperature ($T_r$) at 65 °C. Static force, temperature, and length are plotted as a function of time.

Table D-1. The maximum strain ($\varepsilon_{\text{max}}$), strain upon load removal ($\varepsilon_f$), shape fixity ($R_f$), and shape recovery ratio ($R_r$) for SP-PUR-P and SP-PUR-H when 2 cycles of standard dual-shape memory thermomechanical cycle were performed for each.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>cycle</th>
<th>$\varepsilon_{\text{max}}$ (%)</th>
<th>$\varepsilon_f$ (%)</th>
<th>$R_f$ (%)</th>
<th>$R_r$ (%)</th>
<th>tex</th>
</tr>
</thead>
<tbody>
<tr>
<td>SP-PUR-P</td>
<td>1</td>
<td>68.29</td>
<td>67.23</td>
<td>98.4</td>
<td>92.5</td>
<td>59</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>151.7</td>
<td>149.2</td>
<td>98.4</td>
<td>96.4</td>
<td>47</td>
</tr>
<tr>
<td>SP-PUR-H</td>
<td>1</td>
<td>41.25</td>
<td>40.77</td>
<td>98.8</td>
<td>83.5</td>
<td>55</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>125.6</td>
<td>124.1</td>
<td>98.8</td>
<td>86.4</td>
<td>55</td>
</tr>
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</table>
Table D-2. Ultimate strain and tenacity at break for SP-PUR-P and SP-PUR-M in the undamaged state, right after damage, and after self-healing at 65 °C for various time.

<table>
<thead>
<tr>
<th>Self-healing time</th>
<th>SP-PUR-P</th>
<th>SP-PUR-M</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ultimate strain (%)</td>
<td>Tenacity at break (N/tex)</td>
</tr>
<tr>
<td>Undamaged</td>
<td>919</td>
<td>0.0255</td>
</tr>
<tr>
<td>0 min</td>
<td>99</td>
<td>0.0095</td>
</tr>
<tr>
<td>10 min</td>
<td>363</td>
<td>0.0134</td>
</tr>
<tr>
<td>30 min</td>
<td>840</td>
<td>0.0173</td>
</tr>
<tr>
<td>60 min</td>
<td>737</td>
<td>0.0195</td>
</tr>
<tr>
<td>120 min</td>
<td>841</td>
<td>0.0238</td>
</tr>
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</table>
Figure D-3. Stress-strain curves for A – SP-PUR-P fiber and B – SP-PUR-H fiber after undergoing 1, 2, 3, and 4 cycles of the shape memory cycle. Fibers were deformed at rt. Shape recovery was performed by heating at 65 °C for 10 mins. There was no shape fixation step.
Table D-3. The maximum strain upon deformation, strain after load removal, shape fixity, and shape recovery ratio for SP-PUR-P and SP-PUR-M fibers in each the shape memory cycle in Figure D-3.

<table>
<thead>
<tr>
<th>Shape memory cycle</th>
<th>Fiber</th>
<th>SP-PUR-P (%)</th>
<th>SP-PUR-M (%)</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>Strain upon deformation (%)</td>
<td>800</td>
<td>800</td>
</tr>
<tr>
<td></td>
<td>Strain after load removal (%)</td>
<td>570</td>
<td>750</td>
</tr>
<tr>
<td></td>
<td>Strain after shape recovery (%)</td>
<td>30</td>
<td>55</td>
</tr>
<tr>
<td></td>
<td>Shape fixity (%)</td>
<td>71.3</td>
<td>93.8</td>
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<tr>
<td></td>
<td>Shape recovery ratio (%)</td>
<td>94.7</td>
<td>92.7</td>
</tr>
<tr>
<td>2</td>
<td>Strain upon deformation (%)</td>
<td>800</td>
<td>800</td>
</tr>
<tr>
<td></td>
<td>Strain after load removal (%)</td>
<td>600</td>
<td>620</td>
</tr>
<tr>
<td></td>
<td>Strain after shape recovery (%)</td>
<td>15</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>Shape fixity (%)</td>
<td>75.0</td>
<td>77.5</td>
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<tr>
<td></td>
<td>Shape recovery ratio (%)</td>
<td>97.5</td>
<td>95.2</td>
</tr>
<tr>
<td>3</td>
<td>Strain upon deformation (%)</td>
<td>800</td>
<td>800</td>
</tr>
<tr>
<td></td>
<td>Strain after load removal (%)</td>
<td>580</td>
<td>680</td>
</tr>
<tr>
<td></td>
<td>Strain after shape recovery (%)</td>
<td>10</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>Shape fixity (%)</td>
<td>72.5</td>
<td>85</td>
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<tr>
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<td>Shape recovery ratio (%)</td>
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<td>Strain after load removal (%)</td>
<td>580</td>
<td>680</td>
</tr>
<tr>
<td></td>
<td>Strain after shape recovery (%)</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>Shape fixity (%)</td>
<td>72.5</td>
<td>85.0</td>
</tr>
<tr>
<td></td>
<td>Shape recovery ratio (%)</td>
<td>98.3</td>
<td>98.5</td>
</tr>
</tbody>
</table>
Figure D-4. DMA of SP-PUR-P (A) and SP-PUR-M (B).
REFERENCES


[154] Xie T. Recent advances in polymer shape memory. Polymer. 2011;52:4985-5000.


[181] Davis DA. Spiropyans as color-generating mechanophores: University of Illinois at Urbana-Champaign; 2010.
