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14. ABSTRACT

Self-healing polymers utilizing the Deils-Alder reaction have received considerable attention due the intrinsic healing capability of this crosslink. This research is studying the application of this crosslink in shape memory polymers to create adaptive materials that can respond to stimulus to recover strain and heal fracture. The past few years have seen a surge of research into autonomous materials; however, the resulting techniques are completely passive, cannot sense the presence of damage to allow a controlled response and cannot be performed during operation. To ensure that the structure's health is maintained, it is imperative that viable methodologies be

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Self-healing polymers utilizing the Deils-Alder reaction have received considerable attention due the intrinsic healing capability of this crosslink. This research is studying the application of this crosslink in shape memory polymers to create adaptive materials that can respond to stimulus to recover strain and heal fracture. The past few years have seen a surge of research into autonomous materials; however, the resulting techniques are completely passive, cannot sense the presence of damage to allow a controlled response and cannot be performed during operation. To ensure that the structure's health is maintained, it is imperative that viable methodologies be developed that evaluate the state of the structure while simultaneously providing a means to mitigate damage and recover the material's properties. In order to provide the fundamental materials to achieve such a system, polymers incorporating efficient reversible cycloaddition reactions are being developed. Our efforts have found that the irreversible Diels-Alder (DA) reaction between anthracene and maleimide moieties can be used to achieve healing efficiencies greater than 94% while remaining stable beyond 240 °C. The self-healing polymer being studied here are obtained from liquid monomers allowing the polymerization of bulk samples that yield mechanical properties comparable to other engineering polymers.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

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Received		Paper
04/11/2017	6	Yunseon Heo, Mohammad H. Malakooti, Henry A. Sodano. Self-healing polymers and composites for extreme environments, J. Mater. Chem. A, ( ): 17403. doi: 1,039,018.00
04/11/2017	7	Lisha Zhang, Florian Julé, Henry A. Sodano. High service temperature, self-mendable thermosets networked by isocyanurate rings, Polymer, ( ): 249. doi: 1,039,019.00
04/11/2017	8	Mohammad A Kazemi-Lari, Mohammad H Malakooti, Henry A Sodano. Active photo-thermal self-healing of shape memory polyurethanes, Smart Materials and Structures, ( ): 055003. doi: 1,039,020.00
08/26/2016	5	Yunseon Heo, Henry A. Sodano. Thermally Responsive Self-Healing Composites with Continuous Carbon Fiber Reinforcement, Composite Science and Technology, ( ): 244. doi: 1,015,433.00
09/09/2015	4	Mohammad H. Malakooti, Patrick L. Anderson, Henry A. Sodano. Toughening mechanism of heterogeneous aliphatic polyurethanes, Polymer, (04 2014): 2086. doi: 10.1016/j.polymer.2014.03.002 369,507.00
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04/12/2017	9	Yun Seon Heo, Henry A. Sodano. Development of a Novel Self-Healing Polymer with High Temperature Stability Read More: https://arc.aiaa.org/doi/10.2514/6.2016-1417, AIAA SciTech Forum. 04-JAN-16, San Diego, CA. : ,
04/12/2017	10	Mohammad H. Malakooti, Patrick L. Anderson, Henry A. Sodano. Visualization of Particle-Toughening Mechanism in Transparent Polyurethanes, ASME 2014 Conference on Smart Materials, Adaptive Structures and Intelligent Systems. 08-SEP-14, Newport, Rhode Island, USA. : ,
04/12/2017	11	Henry A. Sodano, Mohammad H. Malakooti. Fracture Modeling of an Embedded Crack in Self-healing Polymers, ASME 2012 Conference on Smart Materials, Adaptive Structures and Intelligent Systems. 19-SEP-12, Stone Mountain, Georgia, USA. : ,
04/12/2017	12	Yunseon Heo, Henry A. Sodano. Thermo-Responsive Shape Memory Self-Healing Polyurethanes and Composites with Continuous Carbon Fiber Reinforcement, ASME 2015 Conference on Smart Materials, Adaptive Structures and Intelligent Systems. 21-SEP-15, Colorado Springs, Colorado, USA. : ,
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Patents Submitted

Shape-Memory-Self-Healing Polymers

Patents Awarded

Awards

Graduate Students

NAME	PERCENT_SUPPORTED	DISCIPLINE
Yunseon Heo	100	Materials Science and Engineering
Mohammad Malakooti	50	Mechanical Engineering
Lisha Zhang	100	Other (Please Specify) - Macromolecular Engineering
Jiajun Lin	100	Other (Please Specify) - Macromolecular Engineering
FTE Equivalent:	**3.50**	
Total Number:	**4**	

Names of Post Doctorates

NAME	PERCENT_SUPPORTED
Mohammad Malakooti	0.50
FTE Equivalent:	**0.50**
Total Number:	**1**

Names of Faculty Supported

NAME	PERCENT_SUPPORTED	National Academy Member
Herny Sodano	0.08	
FTE Equivalent:	**0.08**	
Total Number:	**1**	

Names of Under Graduate students supported

NAME	PERCENT_SUPPORTED	DISCIPLINE
Jason Baum	0	Materials Science and Engineering
John Hunter Spears	0	Mechanical Engineering
Timothy Shankwitz	0	Mechanical Engineering
FTE Equivalent:	**0.00**	
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Scientific Progress

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Technology Transfer

We have filed a patent on our technology and are seeking commercialization opportunities.

Photoresponsive Polymers for Autonomous Structural Materials with Controlled Toughening and Healing

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Abstract

Self-healing polymers utilizing the Deils-Alder reaction have received considerable attention due the intrinsic healing capability of this crosslink. This research is studying the application of this crosslink in shape memory polymers to create adaptive materials that can respond to stimulus to recover strain and heal fracture. The past few years have seen a surge of research into autonomous materials; however, the resulting techniques are completely passive, cannot sense the presence of damage to allow a controlled response and cannot be performed during operation. To ensure that the structure's health is maintained, it is imperative that viable methodologies be developed that evaluate the state of the structure while simultaneously providing a means to mitigate damage and recover the material's properties. In order to provide the fundamental materials to achieve such a system, polymers incorporating efficient reversible cycloaddition reactions are being developed. Our efforts have found that the irreversible Diels-Alder (DA) reaction between anthracene and maleimide moieties can be used to achieve healing efficiencies greater than 94% while remaining stable beyond 240 °C. In addition to DA based self-healing, this research has identified aromatic isocyanates as self-healing polymers for extreme temperatures. This mendable thermoset polymer is synthesized using commodity reactants through the formation of an isocyanurate-oxazolidone network which exhibit a high service temperature as shown by their T_g of 270 °C and T_d of 365 °C. We demonstrate that this network polymer is repeatedly self-mendable in the presence of a macroscopic crack, yielding considerable recovery of the polymer's strength after thermal annealing. This self-mending behavior is derived from a high density of mechano-responsive isocyanurate rings which are introduced as cross-links in the network. The self-healing polymer studied in this program were obtained from liquid monomers allowing the polymerization of bulk samples that yield mechanical properties comparable to other engineering polymers.

1. Introduction

Self-mendable, or self-healing polymer materials have shown promise as structural materials in situations where material repair is difficult or not possible after the formation of micro or macroscopic cracks.[1, 2] This class of materials has many potentially promising applications; however, many self-healing mechanisms developed over the past decade have focused on low modulus polymers where the chains exhibit a high degree of flexibility to overcome steric issues. Here, we report a new mending chemistry that yields high modulus polymers with stability in extreme temperatures, which have application to engineered materials that require high mechanical strength, stiffness and toughness. Self-healing polymers are mainly based on two different mechanisms. One mechanism, called extrinsic healing, works by filling healing agents in capsules[3] or vascular channels.[4, 5] Examples of healing agent systems include PDMS with tin-based catalysts,[6] epoxy resin and amine-based curing agents,[7, 8] epoxy and mercaptan[9] and dicyclopentadicne.[10] After a crack is initiated and passes through a capsule or vascular channel, the healing agent is free to flow from the vesicle and polymerize to heal the crack. Despite the healing performance, empty capsules or vascular channels are left as defects in the material, which can negatively impact the mechanical properties of the overall structure. Also, in the case of capsules the material is not healable once the fractured location has exhausted its healing agent.

The second mechanism is called intrinsic healing, which is based on a reversible chemical reaction. Reversible Diels–Alder (DA) reactions between for example, maleimide (M) and furan (F)[11,12] or M and anthracene (A)[13-15] have been broadly studied and demonstrated to hold great potential for self-healing. Wudl et.al[11] first reported a novel self-healing polymer based on the DA mechanism, which showed a healing efficiency of 57% using the reversible F-M DA reaction. Heo and Sodano[14] incorporated the F-M adducts into a polyurethane and obtained a healable polymer that utilized the shape memory effect of polyurethane to achieve repeatable healing without an external load, with a very high recovery rate of fracture toughness of 86% obtained. Compared to extrinsic healing polymer materials, intrinsic healing polymer materials based on the DA reaction are easier to prepare and can be healed repeatedly. However, the retro-DA reaction takes place at roughly 120°C,[11] which results in the cleavage of F-M adducts, resulting in a significant drop of mechanical properties due to the loss of F-M cross-links. This chemical instability at temperatures above 120°C somewhat limits the application of the self-healing polymers based on F-M DA adducts with useful temperatures falling below 100°C.[11] More recently, 9-anthracenemethanol, has been used as a substituent for furan in the DA reaction to achieve a higher cleavage temperature thus expanding the application space of these polymer materials.[14,15] Due to the high cleaving temperature of >250°C,[16, 17] thermal cleaving cannot be used to assist in healing when the cleaving temperature of A-M DA adducts is beyond the decomposition temperature of the polymers, therefore self-healing polymers based on thermally induced retro-DA reaction between A and M have not been reported yet. Existing healing concepts are based on the mechano-chemical cleavage of A-M DA adducts, followed by thermally initialing the forward DA reaction to reform the mechanically cleaved DA linkages.[14,15] Although, these developed polymers have a T_g below 65°C, somewhat limiting their application space.[14,15] The use of polymers with a low T_g has limited their application in structural applications because of the significant loss of strength above the T_g.[16] Thus, the development of self-healing polymers which exhibit a higher T_g is needed such that they can be used at the increased temperatures often required in high performance applications.

Other intrinsic self-healing mechanisms besides DA reaction were also developed with excellent healing performance despite the low mechanical strength, which limits their application in the field of structural materials. Matyjaszewski et.al[17] reported a self-healing gel by incorporating reshuffling trithiocarbonate units in a flexible poly (n-butyl acrylate) matrix, whose high chain mobility played an important role in the 94% recovery of tensile modulus for the healed sample. A self-healing rubber based on siloxane equilibration recovered 87% of its initial fracture toughness after healing at 90°C for 24h following the cracking.[18] As we discussed above, challenges that still exist in the development of intrinsic healing strategies to broaden the application of self-healing polymer materials include: (1) polymers that remain chemically stable under extreme environments; (2) polymers with a high T_g that maintain their high mechanical strength under elevated temperatures; (3) polymers with excellent mechanical properties comparable to engineering plastics. Here, it is shown for the first time that mechanically cleaved isocyanurate rings can be reformed to recover the polymer's fracture toughness, while also forming a densely cross-linked polymer network that yields high glass transition temperature (T_g) and onset decomposition temperature (T_d); and both the tensile strength and Young's modulus of the polymer are within the range of those reported for composite grade epoxies.[21]

1.1 Self-Healing Through Diels-Alder (DA) Cycloaddition

Reversible Diels-Alder (DA) cycloaddition is one of the most promising and commonly selected mechanisms used in intrinsic self-healing systems due to the reaction's simplicity, reversibility, and repeatability. However, the thermally reversible nature of the DA reaction places limitations on the practical use temperature of the polymer making it poorly suited as an engineering material for high performance applications. Here, it is shown that the retro Diels-Alder (rDA) reaction is not required for healing and that a high healing efficiency of polymers and polymeric composites in addition to their thermal stability beyond 240 °C can be repeatable attained using a DA reaction between anthracene and maleimide molecules. This is possible since crack propagation can be controlled due to the bond energy of the C-C σ bonds from the DA reaction being lower than the energy of the other covalent bonds. From the literature, the C-C crosslinking bond energy between anthracene and maleimide varies from 77 kJ/mol to 117 kJ/mol depending on the attached substituents while the rest of the covalent bond energies are 348 kJ/mol for C-C bonding, 389 kJ/mol for N-H bonding, and 293 kJ/mol for C-N bonding. Thus, the crack requires lower energy to propagate through these new C-C σ bonds, which can be reformed after scission, providing a mechanism for self-healing and recovery of the polymer's original properties.

Furan and maleimide groups have been the most used diene and dienophile candidates for developing Diels Alder based self-healing polymer systems since they are highly reactive due to their low reaction energy.[11,12] The high reactivity is due to the electron withdrawing ketones in maleimide and furan's locked *cis* conformation that is thermodynamically less stable due to steric repulsion and therefore, more reactive. However, the major limitation of using these moieties is the relatively low application temperature range due to the cleaving rDA reaction, which occurs at approximately 120 °C.[11] This is a critical limitation for higher temperature applications (greater than roughly 130 °C) since the polymer may become unstable, degrade or experience a significant drop in Young's modulus above the cleaving temperature due to the loss of crosslinking bonds. In an effort to expand the useful temperature range of self-healing polymers, DA/rDA reactions using anthracene as a diene have been investigated,[13-15] since the rDA reaction theoretically proceeds between 250 °C and 300 °C.[16, 17] Therefore, self-healing polymers with anthracene and maleimide should be very stable under exposure to high temperatures. However, this temperature range is above the decomposition temperature of the anthracene and maleimide monomers and therefore, researchers have never experimentally proved cleaving occurs. Furthermore, due to the decomposition of the individual molecules, these moieties have never been shown to exhibit high self-healing efficiency (above 60%) through the reversibility of the DA reaction.[16, 17] Although it was previously shown that the dissociation of the anthracene–maleimide adducts can be used to synthesize healable and thermally stable polymers, this potential has not been fully achieved yet. Low healing efficiency (only 27% recovered elastic modulus) and very slow healing progress at an elevated temperature (healing treatment for 3 days at 100°C) were the major drawbacks for this DA base self-healing polymer. Here it is shown that through the reformation of the DA bonds in a polymer networks it is possible to synthesize high strength self-healing polymers with superior and repeatable healing ability. Additionally, this is the first demonstration of the use of DA adduct between anthracene and maleimide in fabrication of self-healing composites with a healable DA polymer matrix that exhibits both mechanical and thermal stability.

Self-healing DA based polymers and mendable carbon fiber reinforced polymer (CFRP) matrices were synthesized that exhibit excellent thermal stability and mechanical properties. The realization of a liquid resin formed through the pre-polymerization between the precrosslinked adducts of 9-anthracenemethanol and N-(2-hydroxyethyl)-maleimide (HEM) and hexamethylene diisocyanate (HDI) facilitates fabrication of bulk polymer specimens and CFRP composite layup. Unlike the past research on DA adduct between anthracene and maleimide, the proposed solvent-free pre-polymerization reaction leads to the synthesis of thermally stable DA polymers with a fast-paced, repeatable, yet high healing efficiency.[9, 13] These favorable characteristics of the synthesized polymer are suitable for the development of mendable fiber reinforced polymer composites. Thus, using this thermally stable self-healing polyurethane as a polymer matrix, healable CFRP composites for high-temperature structural applications are fabricated through vacuum assisted resin transfer molding (VARTM). The healing efficiencies of the bulk polymer samples and CFRP composites are characterized using compact tension and short beam shear testing, respectively. Moreover, the mechanical properties of the developed self-healing polymer and CFRP composites are examined in order to evaluate their structural performance.

2. Experimental Methods

2.1. Self-Healing Polymers

2.1.1. Synthesis

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

HEM synthesis: HEM was synthesized through a three step process, starting with maleic anhydride and furan as shown in Figure 1**.** Maleic anhydride (60 g, 612 mmol) and furan (42g, 617 mmol) were initially reacted (DA reaction) in toluene (600 ml) at room temperature to protect the C=C bonds in maleic anhydride prior to the reaction with ethanolamine due to the highly reactive C=C bonds. After reacting them for 24 hours in toluene, the resulting compound (**1**) in Figure 1 was precipitated out and thus, vacuum filtered and washed with diethyl ether. Then, compound (**1**) (60 g, 361 mmol) was reacted with ethanolamine (22 g, 362 mmol) in methanol (120 ml) by refluxing the mixture for 24 hours. When the methanol solution was cooled down to room temperature, product (**2**) was precipitated out and vacuum filtered. The fully dried resulting product (**2**) (60 g) was refluxed in toluene (400 ml) to cleave the furan until the furan peaks at 6.53 ppm and 5.10 ppm were not detected in proton nuclear magnetic resonance (^{1}H NMR). The solution was cooled down to room temperature and the cleaved product (HEM) was crystallized and filtered. All products were fully dried in a vacuum oven for 24 hours before the next reaction was initiated.
Product 1: yield 85.6%, mp 123 °C; ^{1}H NMR (300 Hz, DMSO-d_6) δ 6.59 (s, 2H), 5.36 (s, 2H), 3.32 (s, 2H) ppm; ^{13}C NMR (300 Hz, DMSO-d_6) δ 172.0, 137.3, 82.1, 49.5 ppm. Product 2: yield 46.6%, mp 142 °C; ^{1}H NMR (300 Hz, DMSO-d_6) δ 6.53 (s, 2H), 5.10 (s, 2H), 4.74 (br, 1H), 3.40 (br, 4H), 2.90 (s, 2H) ppm; ^{13}C NMR (300 Hz, DMSO-d_6) δ 176.9, 136.9, 80.7, 57.7, 47.6, 41.1 ppm. HEM: yield 83.0%, mp 75 °C; ^{1}H NMR (300 Hz, DMSO-d_6) δ 6.97 (s, 2H), 4.80 (br, 1H), 3.44 (br, 4H) ppm; ^{13}C NMR (300 Hz, DMSO-d_6) δ 171.5, 134.9, 58.4, 40.4 ppm

Pre-crosslinked compounds (HTDA) synthesis: HTDA was employed in the polymer synthesis process to ensure that all HEM and 9-Anthracenemethanol molecules were fully crosslinked before testing. The synthesis procedures were adapted from Syrett et al.'s work and slightly modified.[3] The synthesized HEM and 9-Anthracenemethanol were refluxed in toluene for 24 hours. Then, the solution was hot-filtered and cooled down to room temperature in order to produce HTDA as shown in Figure 4. Yield 86.4%, mp 185 °C, ^{1}H

NMR (300 Hz, DMSO-d_6) δ 7.74 (d, 1H), 7.44 (d, 1H), 7.19 (m, 6H), 5.40 (t, 1H), 4.91 (q, 2H), 4.74 (d, 1H), 4.68 (t, 1H), 3.29 (m, 2H), 3.08 (t, 2H), 2.66 (m, 2H) ppm, ^{13}C NMR (300 Hz, DMSO-d_6) δ 177.0, 176.2, 143.0, 140.4, 139.9, 126.8, 126.6, 126.3, 125.2, 124.9, 124.1, 122.9, 58.7, 57.0, 49.8, 48.0, 45.9, 45.5 ppm

Polymer synthesis: By using HTDA, TEA, and HDI, two polymers (named 0.5HTDA1T and 0.8HTDA1T) with different compositions were synthesized. To produce 0.5HTDA1T, 0.5 moles of HTDA, 1 mole of TEA and 2 moles of HDI were reacted. Similarly, for 0.8HTDA1T, 0.8 moles of HTDA, 1 mole of TEA and 2.3 moles of HDI were reacted. The steps for this polymerization process can be seen in Figure 2. To synthesize either polymer, the proper molar ratio of HTDA and HDI were reacted at 105 °C for approximately 3 hours until the mixture became completely transparent. The molten resin was mixed with TEA until it became one phase and then quickly poured into a Teflon mold. The mold with resin was degassed for 30 minutes in a vacuum oven at room temperature. Then, the specimen was heated up to 125 °C over one hour and maintained at this temperature for two hours. After that, the specimen was decreased to 90 °C over one hour with a two hour dwell time and finally cooled down to 70 °C over one hour and stayed for another two hours.

Efficiency of DA reaction: Variable temperature proton NMR (VT ^{1}H NMR) was conducted to characterize the kinetics of the DA reaction. In an NMR tube, 1 mole of the synthesized HEM and 1 mole of 9-Anthracenemethanol were mixed in DMSO-d_6 solvent and the mixture was heated at 140 °C to measure the changes in the peaks as soon as the specimen reaches the target temperature of 140 °C (0 minute), and after 5 minutes, 15 minutes, 30 minutes, and 100 minutes.

2.1.2. Healing Efficiency

Healing efficiency was calculated with the modified compact tension testing data values from the two different molar ratio polyurethanes.[1] Two modifications were applied; a resting hole on the crack path was added to stop the crack propagation and the length of pre-crack was reduced. From the CT testing, the maximum loads at fracture were obtained and used to calculate the healing efficiency as the maximum loads of the post-healing specimens divided by the maximum loads of the initial specimens.

2.1.3. Thermal Analysis

In order to investigate the decomposition temperature, TGA (TA Q50) was conducted at a heating rate of 20 °C/min up to 600 °C under a nitrogen condition. Approximately 10 mg of sample was placed on the platinum pan and the balance was purged at 40 mL/min and the sample was purged at 60 mL/min. For the polymer phase changes, DSC (TA Q20) was employed and a 10 mg specimen was placed in a Tzero aluminum pan. The specimen was cooled to -10 °C and then heated to 250 °C with a 10 °C/min ramping rate and 50 mL/min sample purge flow rate under nitrogen condition. All the acquired data from TGA and DSC testing were analyzed on "TA Universal Analysis" software provided by the equipment manufacturer.

2.1.4. Mechanical Properties

Tensile testing and CT testing were conducted to evaluate the properties of the developed polyurethanes[1, 19] and these values were compared to reported commercial epoxy data. In addition, the specimens were heat treated at 160 °C for 20 hours and the heat treated specimens were tested to ensure heat stability as well as heat resistivity. Each test was conducted on four specimens and the average results were reported along with the standard deviations. From the tensile testing, the ultimate tensile strength, strain, and Young's modulus were obtained and the specimens (based on ASTM 638 Type V) were tested at room temperature with an opening rate of 5 mm/min. For the CT testing, the samples (based on the ASTM D 5045) were prepared and examined at room temperature on an Instron 5936 with an opening rate of 5 mm/min.

2.2. Self-Healing Composites

2.2.1. Composite Fabrication

To fabricate the CFRP composites both for self-healing ability testing and mechanical testing, 0.8 moles of HTDA and 2.3 moles of HDI were pre-polymerized at 105 °C for approximately 3 hours until the mixture became completely transparent. The molten resin was mixed with TEA until it became one phase. Then, similar to the previous method,[20] the molten resin at 105 °C was added through one tube while vacuum was applied with the other. In order to transfer the highly viscous resin to the low pressure outlet tube within a short period of time (approximately 30 minutes), Teflon film was employed to reduce the friction between the resin and plate and moreover, the VARTM setup was placed on a 60 °C hot plate. Upon complete resin transfer using VARTM, the layup was subjected to a pressure of ~100 psi. Then, the vacuum bagging layup was heated at 150 °C for three hours on a hot press, followed by heating at 150 °C for two hours in an oven without any pressure to ensure complete polymerization. The short beam shear samples were prepared using 12 plies of unidirectional carbon fiber fabric which resulted in composites with a final thickness between 3.3 mm and 3.4 mm. For preparation of tensile test samples, only 3 plies of unidirectional carbon fibers were utilized for the composite layup which resulted in composites with a thickness of less than 1 mm. For both short beam strength and tensile tests, reference composite specimens with epoxy resin (Epon 862 and curing agent 3230 with a mixing ratio of 100:35) were fabricated in an exact manner but a different curing profile. To fully cure the epoxy phase, the layup was kept at room temperature for 20 hours, followed by heating at 80 °C for two hours, and then post curing at 125 °C for three hours.

2.2.2. Healing Efficiency

The healing efficiencies of the composite samples were calculated using short beam strength data obtained through short beam strength testing. This testing was performed on an Instron 5969. The specimen dimensions and testing procedures were provided by the ASTM D2344 standard. According to the standard, for a specimen with a thickness of 3.3 mm, the prepared specimen should have a width of 6.6 mm and a length of 19.8 mm. A total of 13 specimens were initially tested at room temperature at a rate of 1 mm/min. This process was performed twice more on each specimen to obtain first and second healing cycle efficiencies. After each testing, the healing process was applied on the C0.8HTDA1T specimens. They were heated from room temperature to 160 °C and then kept at the same temperature for two hours. Then, the specimens were cooled down and kept for two hours at 120 °C, followed by 2 hours at 70 °C under a pressure of 100 psi in a hot press. Between the different temperature conditions, an extra 15 minutes was needed to regulate the set temperatures. The healing temperature profile for C0.8HTDA1T was the same as that for 0.8HTDA1T. Moreover, this experimental method was utilized to report the initial shear strength of the short beam self-healing composites to compare it with the shear strength of the composites with epoxy resin.

2.2.3. Mechanical Performance

The tensile properties of the fiber reinforced self-healing polymers and fiber reinforced epoxy composites were examined in accordance with the ASTM D3039. Tensile composite samples were machined to 150 mm by 12.5 mm after completing the composite fabrication process. 15 tensile specimens with self-healing matrix (three sets of fabricated composites) and 10 tensile specimens with epoxy matrix (two sets of fabricated composites) were prepared by adding end-tabs of carbon fiber reinforced composites. The tensile tests were conducted using a cross-head speed of 3 mm/min and a load capacity of 100 kN with an Instron 5982 load frame. To accurately measure the strain along the composite beams, an extensometer with a 25.4 mm gauge length was used. The Young's modulus of the composites specimens were calculated based on the captured strain through the extensometer in the linear portion of the stress-strain curve and the maximum stresses before rupture were utilized to report the tensile strength of each specimen.

3. Results and Discussion

3.1. Self-Healing Polymers

The precrosslinked monomer (HTDA) of 9-anthracenemethanol and N-(2-hydroxyethyl)-maleimide (HEM) was synthesized to ensure that the self-healing agents were fully crosslinked before the crack was introduced. A schematic of the HTDA synthesis process is shown in **Figure 1** and the detailed synthesis procedures can be found in the Experimental Methods.

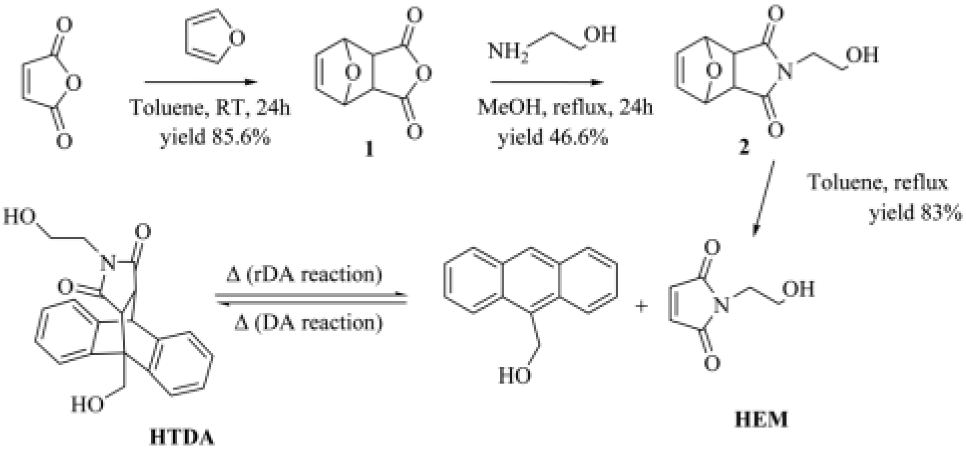

Figure 1. A schematic of the four–step methodology to synthesize healable HTDA monomer.

In order to design solvent-free polymerization method for bulk polymer specimens and matrix phase in resin infused CFRP composites, isocyanate terminated pre-polymer between the HTDA and hexamethylene diisocyanate (HDI) was synthesized first as shown in **Figure 2**. The pre–polymer is a viscous liquid monomer that plays an important role in eliminating the needs of any solvents and thus, all the liquid monomers can synthesize bulk polymer specimens and also be used in composite fabrication. Two polyurethanes were synthesized with different molar ratios of the healing DA molecules such that healing can be correlated to the fraction of reformable crosslinks. The first polymer is designated 0.5HTDA1T and consists of 0.5 moles of HTDA, 1 mole of TEA and 2 moles of HDI and the second, 0.8HTDA1T, is synthesized with 0.8 moles of HTDA, 1 mole of TEA and 2.3 moles of HDI. The second polymer has a greater molar fraction of the healable HTDA molecule and therefore, a better healing performance is expected. A schematic of the polymer network is presented in Figure 2 and detailed chemical information and polymerization methods can be found in the Experimental Methods.

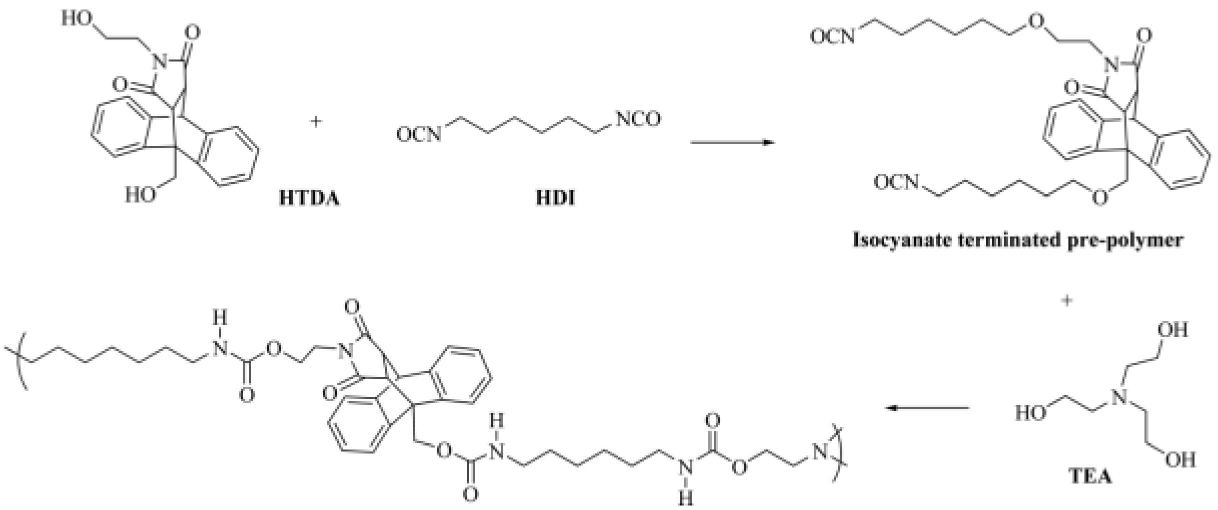

Figure 2. A schematic of the polymerization process with HTDA, TEA, and HDI monomers.

3.1.2. Efficiency and Kinetics of DA reaction

The efficiency and kinetics of this DA reaction was characterized through variable temperature proton nuclear resonance (VT ^{1}H NMR) with 500 MHz magnetic field at the reaction temperature. The reaction was prepared by dissolving the constituents in deuterated dimethyl sulfoxide (DMSO-d_6) solvent and heating to 140 °C by using an internal heating function of the NMR instrument for 0 minute, 5 minutes, 15 minutes, 30 minutes, and 100 minutes. The NMR spectra corresponding to each heating time is shown in **Figure 3**. It can be clearly seen that the peaks approximately at 8.5 ppm, 8.1 ppm, and 7.5 ppm for the anthracene protons and the peak at 7 ppm for maleimide protons disappear from Figure 1a as the duration of heating increases. It can be observed that the DA reaction between anthracene and maleimide progresses relatively quickly at 140 °C, since most crosslinking is shown to be complete after only 5 minutes of heating. The peak at 7 ppm shifts to 6.9 ppm following cycloaddition due to changes in the neighboring protons. Therefore, the efficiency for the crosslinking DA reaction between these molecules is close to 100% since the anthracene and maleimide peaks essentially completely disappear from the VT ^{1}H NMR spectrum.

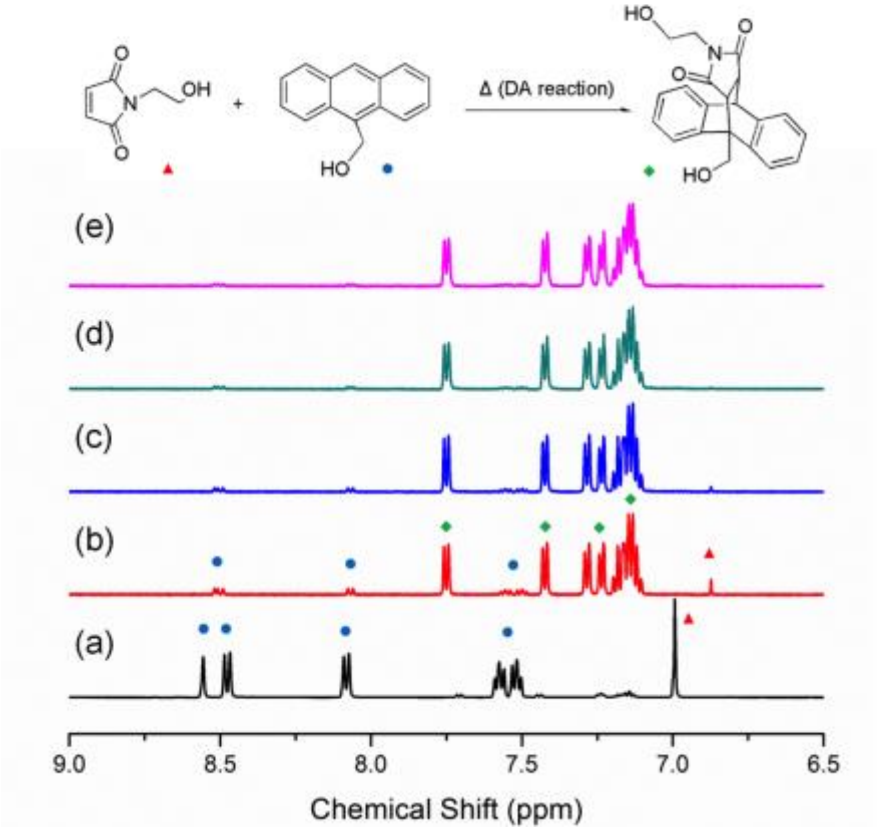

Figure 3. VT ^{1}H NMR spectra for the kinetics of the crosslinking DA reaction; the specimen heating duration at 140 °C for (a) 0 minute, (b) 5 minutes, (c) 15 minutes, (d) 30 minutes, and (e) 100 minutes.

3.1.3. Healing Efficiency

The healing efficiency of the polyurethane has been measured to validate if only the reformation of the broken σ C-C bonds can lead to healing. The healing efficiency was calculated through compact tension (CT) fracture testing in order to obtain the virgin and post-healed maximum loads when the crack is induced. Four of each polyurethane were prepared with a slightly modified ASTM D 5045 configuration by shortening the pre-crack length and by inserting a resting hole to stop crack propagation.[1] These modifications were made to avoid catastrophic failure of the specimen and allow the crack surfaces to maintain their initial position with respect to each other. Following fracture of the specimen, the healing was performed on a hot press with approximately 100 psi of pressure applied. The specimens were heated with a two hour each at 160 °C, 120 °C and lastly 70 °C. The specimens were then removed from the press and heated at 120 °C in an oven under ambient pressure to recover the shape and to eliminate any internal stresses that might have been created from the pressure. Representative fracture of behavior of the 0.5HTDA1T and 0.8HTDA1T samples are shown in **Figure 4**a and 4b, respectively. The healing efficiencies as calculated from eight samples of each condition are provided in **Table 1**, showing that 0.5HTDA1T exhibits a healing efficiency of 66.3%, 70.5% and 62.1% for the first, second and third healing cycles, respectively. The case of a high molar fraction of DA crosslinks lead to significantly improved healing efficiency with the 0.8HTDA1T samples producing a healing efficiency from six averaged specimens of 94%, 78% and 77% for the first, second, and third cycles, respectively. This result shows that a larger molar fraction of HTDA is required to increase the healing efficiency. A high fraction of HTDA is important since it is believed that crack propagation occurs mostly through DA bonds due to its lower bond energy. The C-C crosslinking bond energy between anthracene and maleimide has been reported to vary from 77 kJ/mol to 117 kJ/mol depending on the attached substituents[5] while the rest of the covalent bond energies are 348 kJ/mol for C-C bonding, 389 kJ/mol for N-H bonding, and 293 kJ/mol for C-N bonding.[6] However, it is probable that the crack can propagate through a number of covalent bonds that cannot be recovered and thus the efficiencies for both polymers were not expected to reach 100%. In each subsequent fracture and healing cycle, more covalent bonds were damaged resulting in a decreasing healing efficiency, especially in 0.8HTDA1T. In contrast to 0.8HTDA1T, 0.5HTDA1T shows a nearly constant healing efficiency, which is attributed to the lower fraction HTDA moieties resulting in more significant covalent bond damage and thus creating a pathway for crack propagation. With the high crosslinking efficiency of the HTDA, it is expected that the nearly constant fracture strength is solely a result of the reformed HTDA crosslinks. Figure 4c shows a photograph of the fractured 0.8HTDA1T specimen (left) with a clearly visible crack and following healed specimen (right), clearly demonstrating the reformation of the bonds in polymer with the vanished fracture surfaces.

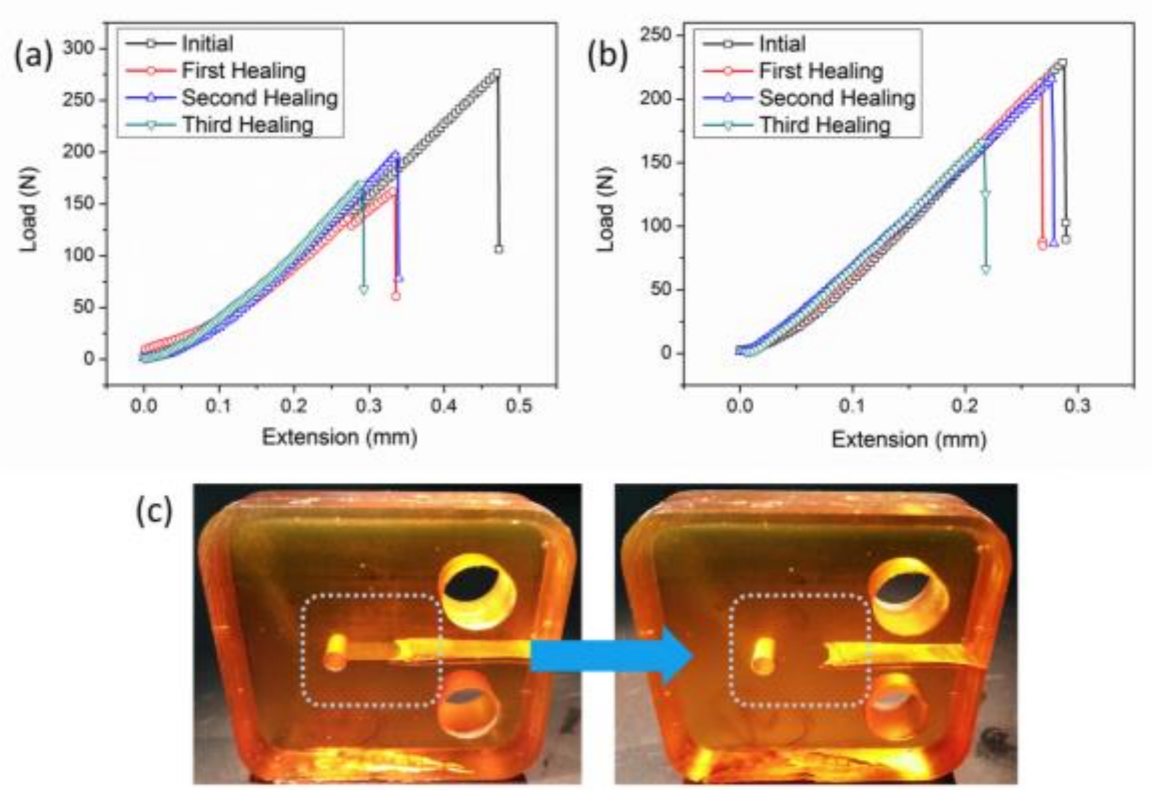

Figure 4. Representative load curves as a function of extension for one, (a) 0.5HTDA1T and (b) 0.8HTDA1T specimen, and (c) one 0.8HTDA1T specimen showing pre- (left) and post-healing (right).

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

Polyurethane	Healing Efficiency$^{a)}$ (SD)		
	1st cycle	2nd cycle	3rd cycle
0.5HTDA1T	66.3% (14.2)	70.5% (14.1)	62.1% (15.1)
0.8HTDA1T	94.4% (14.4)	77.8% (16.7)	76.7% (9.7)

$^{a)}$ Percentage of healing ability was determined as the ratio of the post-healed maximum load to the initial maximum load.

3.1.4. Thermal Stability

The thermal stability of the self-healing polymers has been investigated through thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) on two samples of each polymer. The weight loss curves obtained from TGA are shown in **Figure 5**a and demonstrating that the polymer does not decompose until the temperatures reaches to 251 °C for 0.5HTDA1T and 240 °C for 0.8HTDA1T. Even beyond the T_g, both polymers were stable and thus, applicable in the high temperature working conditions up to 240 °C. As mentioned earlier, one major limitation of self-healing polymers using maleimide and furan molecules for the reversible DA reaction is to contain the low cleaving temperatures (around 120 °C). These polymers would considerably degrade when they are heated above their cleaving temperature through thermally induced cleavage of the DA bonds. The DSC data in Figure 5b shows no sudden heat flow transitions as a function of temperatures up to 250° C, thus indicating the polymers do not experience cleaving reactions below this temperature. These TGA and DSC data demonstrate that the healing response is not a functional of thermally induced cleavage but mechanically induced cleavage of the DA bond following by reformation upon application of thermal energy. It is noted that the healing response may occur at room temperature and therefore healing micro cracks and preventing the onset of critical damage. However, under the macroscopic fracture conditions studied here, the crack sterically hinders the reformation of the bond.

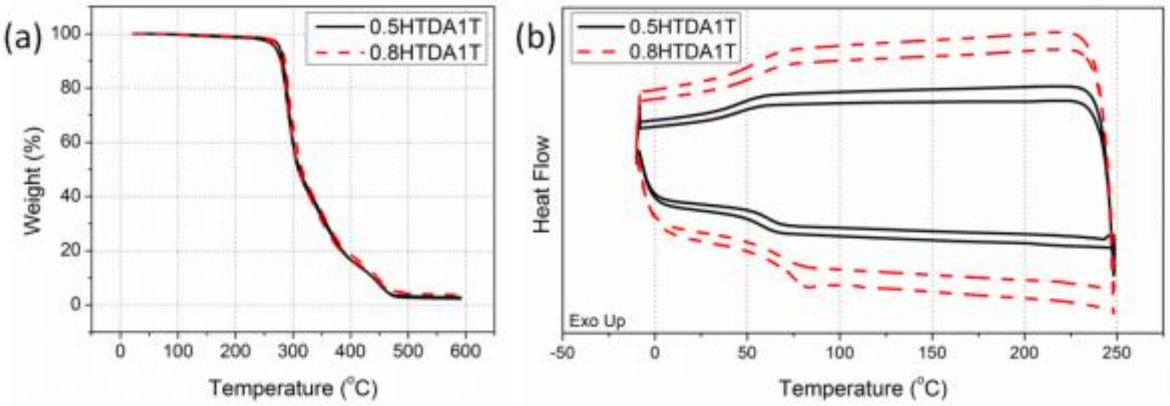

Figure 5. (a) TGA curves for decomposition temperatures and (b) DSC curves for phase stability up to 250 °C.

3.1.5. Mechanical stability

The mechanical stability of the self-healing polymer processed under a high temperature has been evaluated in order to ensure that the polymer does not degrade due to the prolonged heat exposure. Therefore, mechanical testing was performed before and after annealing the polymer at 160 °C for 20 hours under a nitrogen atmosphere. As depicted in **Figure 6**, the tensile strength, elastic modulus, and fracture toughness of the both polymers do not decrease after the heat treatment. In fact, the average values of these mechanical properties slightly improve during this process. For instance, the average tensile strengths of the polymers are improved about 8% while the measured elastic moduli remain relatively constant before and after the heat treatment. The improved strength and toughness may be a result of further crosslinking, increased crystallinity and also the relaxation of internal stresses or micro voids in structures from curing.[14] Accordingly, the annealed polymer structure helps to enhance the strength and toughness which are reflected in the mechanical properties. This observation clearly demonstrates that both synthesized self-healing polyurethanes (0.5HTDA1T and 0.8HTDA1T) do not degrade under continuous heating.

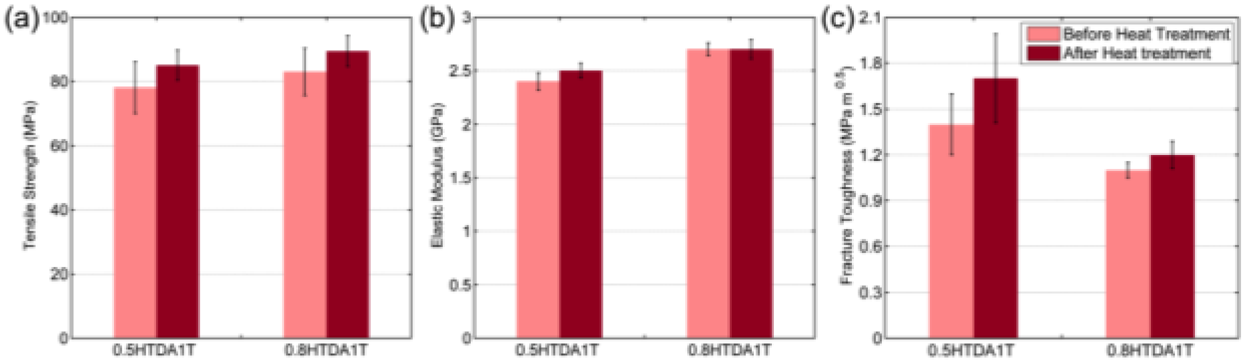

Figure 6. Comparison between mechanical properties of 0.5HTDA1T and 0.8HTDA1T before and after heat treatment at 160 °C for 20 hours in an inert condition; (a) tensile strength (b) elastic modulus, and (c) fracture toughness. (The dark-colored bars indicate the mechanical properties after heat treatment)

In order to ensure that the mechanical properties of the polymers, before and after heat treatment, are comparable to other engineering polymers, these properties are compared to the ones of epoxy in **Table 2**. The polymers exhibit structural performance equivalent to aerospace grade epoxies and the author's previously developed self-healing polyurethane (1.5DA1T)[1] with higher heat resistance. Besides the healing capability of the synthesized polymers, their resistance to the applied heat makes them a promising candidate for applications where temperature environments reach as high as 160 °C. One possible use of these high temperature polyurethanes is fabrication of self-healing composites that can stand a large amount of applied mechanical and thermal loading. In the following section, 0.8HTDA1T is utilized as a healable matrix to demonstrate the fabrication of high strength carbon fiber reinforced composites with repeatable healing ability.

Table 2. Mechanical properties and standard deviation (SD) of each polyurethane before and after heat treatment

Property	**0.5HTDA1T (SD)**		**0.8HTDA1T (SD)**		**1.5DA1T (SB)[1]**	**Epoxy**
Heat treatment*	**Before**	**After**	**Before**	**After**		
Ultimate tensile strength (MPa)	78.1 (8.0)	85.0 (7.3)	83.0 (4.8)	89.4 (4.7)	87.8 (7.6)	35-130[15]
Ultimate tensile strain (%)	11.5 (6.9)	8.6 (3.8)	4.1 (0.7)	5.0 (1.2)	5.4 (2.8)	2-5[16]
Elastic modulus (GPa)	2.4 (0.08)	2.5 (0.07)	2.7 (0.06)	2.7 (0.09)	2.6 (0.2)	2-6[15]
Glass transition temperature (°C)	49.6 (3.2)	52.3 (2.7)	52.8 (1.4)	64.1 (9.8)	45.6 (3.8)	50-250[15]
Fracture toughness (MPa·√m)	1.4 (0.2)	1.7 (0.3)	1.1 (0.05)	1.2 (0.09)	1.1 (0.04)	0.65[17]

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

3.2. Self-Healing Composites

Another advantage of the self-healing polymer reported here is that all monomers are liquid phase therefore allowing the fabrication of mendable fiber reinforced polymer composites through the widely used resin transfer process. To integrate healing function into CRFP composites, unidirectional carbon fabrics were infused with the developed self-healing polyurethane (0.8HTDA1T) using vacuum assisted resin transfer molding (VARTM). The healing efficiency of the composites were evaluated and their structural performance was compared to similar composites with epoxy matrix. As verified through nitric acid digestion according to ASTM D 3171 procedure A, the VARTM method yields high volume fraction composites [18] (71% fiber and 29% resin for C0.8HTDA1T by volume).

3.2.1. Healing Efficiency of Composites

The healing efficiency of the composite was evaluated by measuring the short beam strength (SBS) of the specimens before and after healing process of the matrix. In this test, it is assumed that the specimen mid-plane undergoes a failure and cracks propagate through the matrix and fibers in this plane. The load-extension curves of a single short beam specimen subjected to initial loading and two healing cycles is shown in **Figure 7**a. The average healing efficiencies of the composites after first and second healing process are presented separately in Figure 7b. The mendable composites achieved average efficiencies of 69.1% and 52.4% for the first and second healing cycles, respectively.

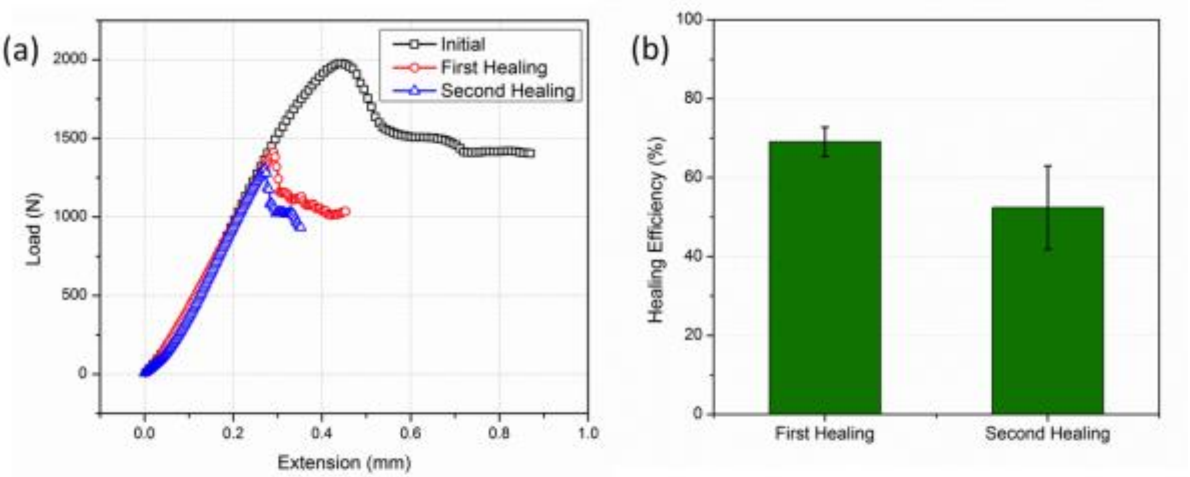

Figure 7. (a) An example of short beam strength testing result for C0.8HTDA1T and (b) the average healing efficiencies for the first and second healing cycles

It is noticeable that the healing efficiency of the composites fabricated from 0.8HTDA1T is not as high as pure polymer CT specimens. The nonhomogeneous structure of the composite can be considered as the main reason of their lower healing efficiencies compared to the homogeneous bulk polymers. In order to investigate the effect of the presence of the carbon fibers and other plausible reasons of lower efficiencies of composites, the damage region resulted from the SBS testing was studied using a scanning electron microscope (SEM, TESCAN VEGA3 LM). **Figure 8**a shows a cross-sectional view of the fractured short beam which was polished before testing. As depicted in the SEM image, the defects likely occurred in two areas; through the polymer matrix region along the direction of the carbon fibers (Figure 8b and 8d) and at the interface of the matrix and glass fibers tow (Figure 8c).

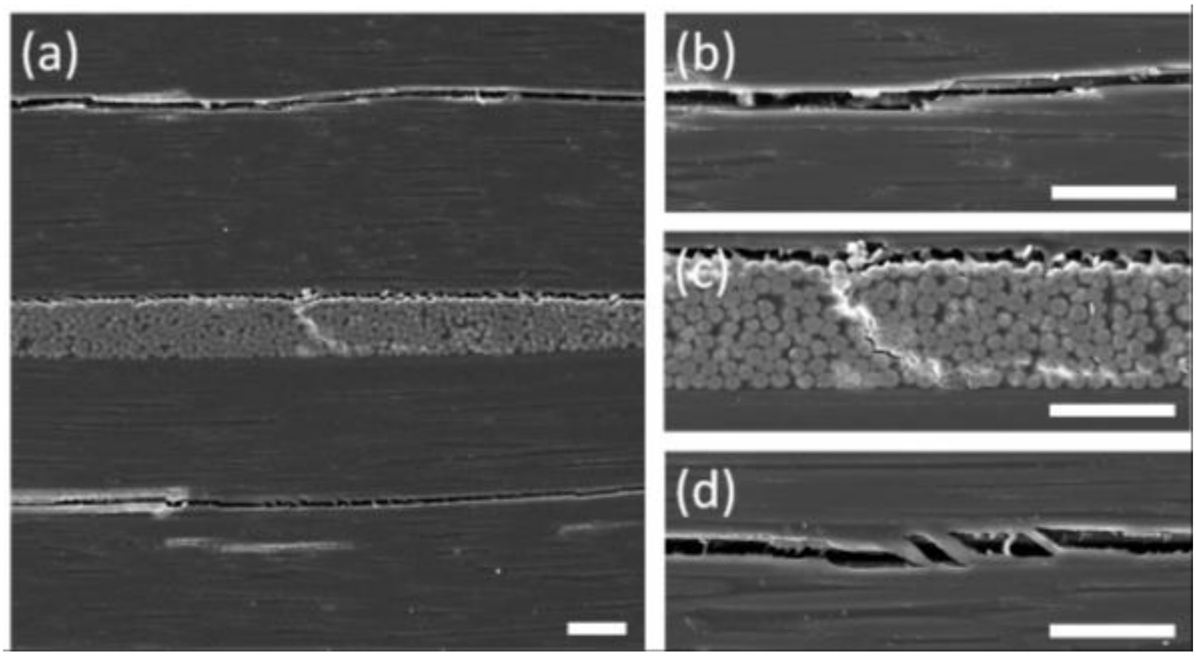

Figure 8. Cross-section micrographs of the self-healing composite (C0.8HTDA1T) showing a) four different damages from SBS testing, b) carbon fiber damage, c) delamination between glass fibers and also glass fiber damage, and lastly d) delamination between carbon fibers. Scale bar: 50μm.

The reduced healing efficiency of the composites compared to the bulk self-healing polymers can be explained through the following reasons. The first and main reason is the failure of the fibers as the primarily load bearing components in the composite that cannot be repaired and results in a drop in the short beam shear strength of the composites after healing cycles (Figure 8b). The delamination of the interface between reinforcing fibers and the polymer matrix is another major reason that leads the reduced healing efficiency due to the absence of a bonding mechanism between fibers and polymer phase (Figure 8c). Moreover, the resulting cracks created through the polymers were healed via the DA reaction; however, in order to completely heal the internal cracks in the composites, the carbon fibers are required to remain in their original positions before the fracture. Therefore, the presence of the voids due to misplaced fibers and loose contact between the fracture surfaces might also contribute to the reduced healing performance of the composites.

3.2.2. Structural Performance of Composites

After evaluating the healing performance of the composites, the load bearing capability of the self-healing composites were compared to the composites with epoxy matrix by conducting shear beam strength and tensile testing. The unidirectional fiber fabrics were infused with structural grade epoxy matrix (Epon 862 and curing agent Epikure 3230) to fabricate reference specimens. As shown in Figure 9a, the average shear strength of the self-healing composites is 69.6 MPa which is about 7% higher than the average shear strength of the epoxy composites (65.2MPa). The higher shear strength of the self-healing composites can be due to either the higher elastic modulus of the polyurethane as the matrix phase or better bonding between the matrix and carbon fibers. A similar trend was observed in the measured elastic modulus of the composites composed of three plies of unidirectional carbon fibers. Loading the tensile specimens along the fibers direction resulted in the average elastic modulus of 138.6 GPa for self-healing composites and 127.7 GPa for epoxy composites (as shown in Figure 9b). Self-healing composites demonstrate slightly higher elasticity (~8.5%) which further confirms the influence of the strength of the used polymer matrix on overall elastic modulus of the composites. However, the high viscosity of the self-healing polymer, compared to the one of the epoxy matrix, resulted in slight defects in the fabricated composites that caused the premature failure of these composite specimens. Therefore, as shown in Figure 9c, the average tensile strength of these composites (1800 MPa) was determined to be about 10% lower than the tensile strength of reinforced epoxy composites (2000 MPa). Nevertheless, the results obtained from mechanical assessment of the composites demonstrated that the developed mendable fiber reinforced composites have a comparable structural performance as common fiber reinforce epoxy matrices.

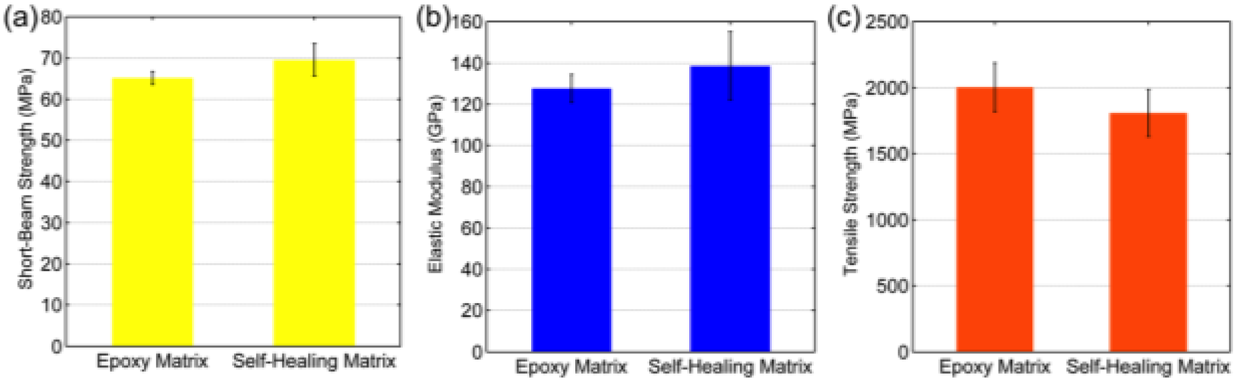

Figure 9. Mechanical properties of self-healing composites compared to unidirectional fiber reinforced epoxy composites: (a) short beam strength, (b) elastic modulus, and (c) tensile strength.

4.0 Extreme Temperature Self-Healing

Some challenges still exist in the development of intrinsic healing strategies. These challenges include: (1) polymers that remain stable and own good mechanical prosperities under elevated temperature; (2) selected reversible bonds that break under a high stress and can reform later to yield healing performance; (3) dense reversible bonds that can be introduced into a polymer matrix to generate a significant molar fraction of reactive groups at the crack surfaces. Our recent efforts have shown for the first time that mechanically cleaved isocyanurate rings can be reformed to produce high healing efficiency, while also forming a densely crosslinked polymer network that yields high glass transition temperature (Tg) and onset decomposition temperature (T_d). Three isocyanurate-oxazolidone (ISOX) polymers (referred to 1TDI/1Epon, 1.5TDI/1EPON and 2TDI/1Epon) are synthesized to study this new healing chemistry and the trimers of isocyanates, termed isocyanurate rings (6-member-ring) are shown to be mechanoresponsive bonds as shown in Figure 10. Isocyanurate rings are embedded with increasing density for 1TDI/1Epon, 1.5TDI/1EPON and 2TDI/1Epon in the network with the T_d reaching 388ºC and the Tg reaching 281ºC. To the best of the PI's knowledge, this is the first instance an isocyanurate ring is shown to act as a repairing moiety. The mending concept derives from the cycloreversion of isocyanurate rings predominated under mechanical stress in solid state. This deformation generates free isocyanates at crack surfaces, which polymerize under thermal stimulus to reform the polymer network across the crack face and return the strength to the polymer as shown schematically in Figure 10. Due to brittle nature of isocyanurate rings [21], Bisphenol F was introduced to produce oxazolidone (5-member-ring), as a chain extender in the network, which imparts improved toughness to the polymer.

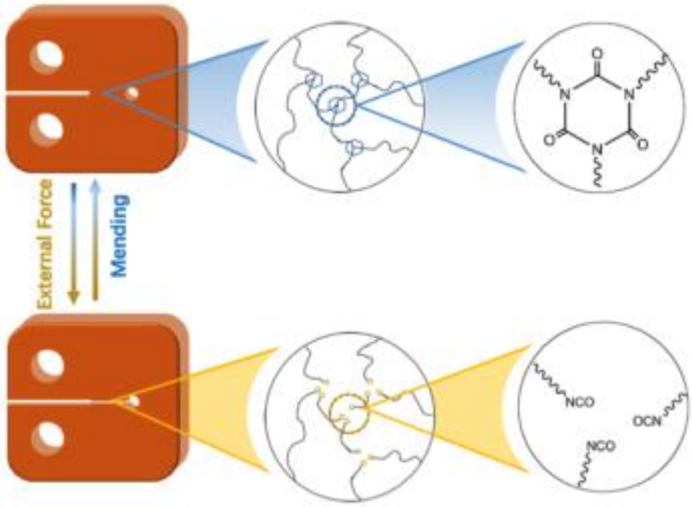

Figure 10. Self-Healing mechanism of the isocyanaurate group.

Following polymerization of the TDI and Epon 862 at 80ºC the specimens showed a strong characteristic peak of the isocyanurate ring at 2260 cm^{-1} and epoxide at 910 cm^{-1}. Initial 1TDI/1Epon, 1.5TDI/1Epon and 2TDI/1Epon samples were gained after 20 h annealing at 200ºC in a hot press. Annealing was expected to release residual stresses in the polymer and produce improved mechanical properties. ATR-IR was used to verify the polymerization process (Figure 11). For cured samples, the peak at 2260 cm^{-1} completely disappears, and new peaks appear at 1710cm^{-1} attributed to the isocyanurate ring (6-member-ring), 1750cm^{-1} for oxazolidone (5-member-ring) and 1100 cm^{-1} for ether. This change in spectra confirmed the formation of the polymer network via trimerization of isocyanates to isocyanurate rings[29, 30] and the formation of ……. epoxy rings.

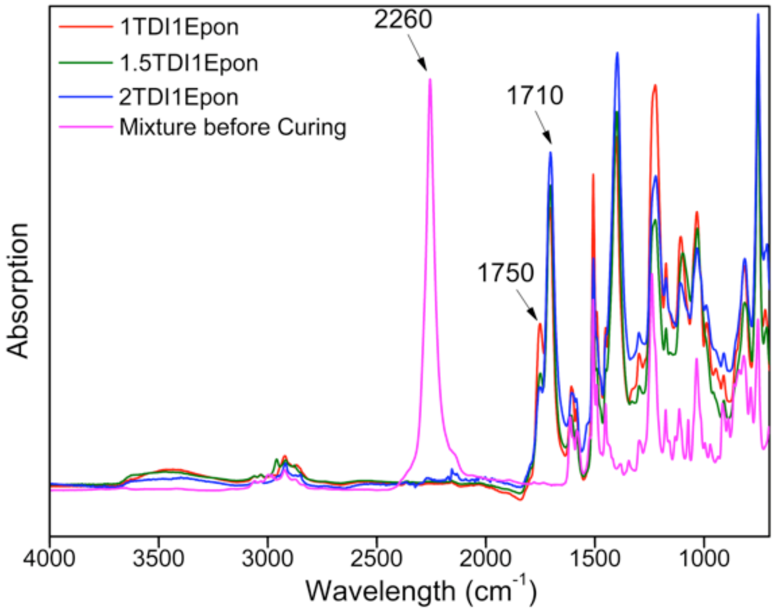

Figure 11. ATR-IR Spectra of Cured Samples of 1TDI/1Epon, 1.5TDI/1Epon and 2TDI/1Epon.

The healing performance of 1TDI/1Epon, 1.5TDI/1Epon and 2TDI/1Epon were evaluated through compact tension (CT) tests. The maximum load to induce fracture in the original samples, first mended samples, second mended samples and third mended samples were recorded and used to calculate the mending efficiency. The mending efficiencies were obtained according to Eq. (1) using the initial and post mended maximum loads. The first, second, and the third mending efficiencies for 1TDI/1Epon samples were 43.52%, 31.63% and 26.49%, respectively; for 1.5TDI/1Epon samples, they were 49.33%, 33.38%, and 32.55%, respectively; for 2TDI/1Epon samples, they were 50.98%, 42.00%, and 42.85% respectively, with the error bars representing the standard deviation shown in Figure 12.

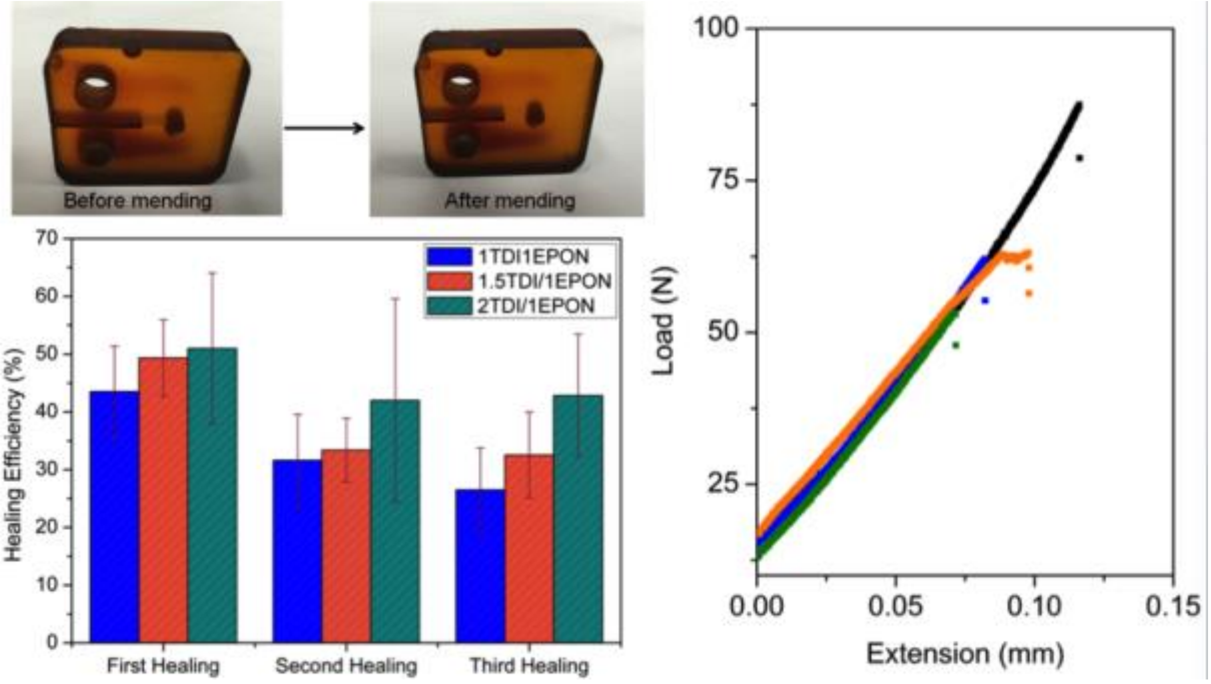

Figure 12. (A) Average Healing Efficiencies of 1TDI/1Epon, 1.5TDI/1Epon and 2TDI/1Epon for the first, second and third healing (B) Comparison of opened sample and mended sample (C)-(E) Examples of failure load plot for 1TDI/1Epon, 1.5TDI/1Epon, and 2TDI/1Epon respectively.

Two possible explanations for why the mending efficiencies of these samples cannot reach 100% exist. One explanation is that the rupture of bonds induced by external mechanical force is not 100% from bonds of isocyanurate rings. Large external stress leads to the unselective scission of covalent bonds in the network, resulting in presence of a crack (Fig.3). Other bonds such as N-C bonds that connect isocyanurate rings to the benzene rings can also be ruptured. Thus, irreversible bond breakages may partially account for the loss in mending efficiency. The second explanation is that every time a specimen is fractured, the crack in the specimen becomes sharper; thus, a higher stress concentration exists in the specimen.

4.1 Analysis of Healing Kinetics

Several tests using used ATR-IR spectrometry were performed in order to prove the hypostasized healing mechanism. The first experiment sought to show that polymer diffusion across the crack face was not responsible for the observed healing eliminates the effects of polymer chain diffusion. A 2TDI/1Epon specimen was used since it has the highest concentration of iscyanurate cross links in the polymer matrix. The sample was prepared with the same method but was fractured completely instead of ceasing the crack growth at the resting hole. The sample was then placed in the oven under a nitrogen atmosphere at 80ºC for 1 h and subsequently post cured for 200ºC for 20 h before the two separate pieces of the fractured CT specimen were put together under pressure and the mending procedure was applied. After cooling down to room temperature, the visual presence cracks of all three specimens of the sample were obvious, and the sample showed little to no healing of the mechanical properties. This observation eliminates the possibility that diffusion of the polymer across the face of the crack. The second experiment used ATR-IR to study the chemistry of the polymer surface and identify the presence of reactive groups that yield healing. In order to perform ATR-IR the CT specimens were fractures completely without a resting hole and the subsequently healing however prior to each healing the fracture surface the IR spectrum was collected as shown in Figure 13. After each mending treatment, the presence of the crack could not be visibly detected and specimen exhibited excellent mechanical properties. From the IR-spectrum in Figure 13, it can be seen that the isocyanate peak at 2260cm^{-1} is be observed in the fracture surface but not in the bulk surface before fracture of the specimen. This result demonstrates that during fracture of the specimen the mechanical stress leads to a scission of the isocyanurate ring leaving free isocyanates, which during healing react to reform the isocyanurate cross link and mend the crack.

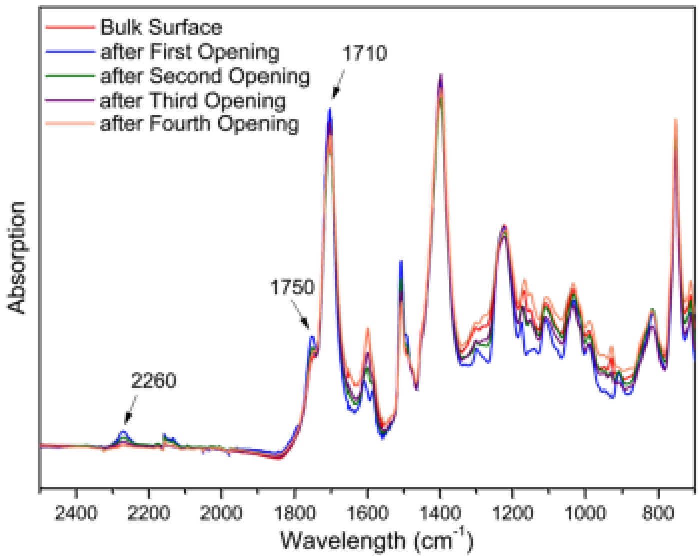

Figure 13. IR spectrum of CT specimen after fracture showing the appearance of isocyanate groups at 2260cm^{-1}.

The third test sought to further evaluate the healing behavior of the isocyanurate group by pulverizing samples into a powder such that the surfaces before and after healing could be observed through ATR-IR spectroscopy. A sample of 2TDI/1Epon was pulverized and subsequently ground into fine powder in a mortar pestle for 30 min to create a high density of fracture surfaces allowing the IR-spectrum to identify the structural change with greater fidelity. The IR-Spectrum is shown in Figure 14 with the ground 2TDI/1Epon showing that upon grinding the surface an isocyanates peak at 2260cm^{-1} appears while the bulk specimen shows no apparent isocyanates. The ground sample was then placed in the oven under nitrogen atmosphere at 80°C for 1 h, and then post cured at 200°C for 20 h to simulate the mending treatment of the bulk sample. Through the mending stage, the powder sample transferred from a state of powder to and aggregated mass and was then tested with ATR-IR spectroscopy showing the isocyanate peak at 2260cm^{-1} completely disappears following the mending step. Then the aggregated mass was then ground for a second time for 30 min before retesting, at which point the isocyanate peak at 2260cm^{-1} was once again observed. The same grinding and mending treatments were applied successively with the disappearance and reappearance of the isocyanaurate peak at 2260cm^{-1} being repeatable. This repeatable cycle indicates the mechanochemical cycloreverison of isocyanurate rings. The reversibility of this mechanical degradation surely contributes to the mending process including the disappearance of the crack and the recovered fracture toughness of the polymers (Figure 12).

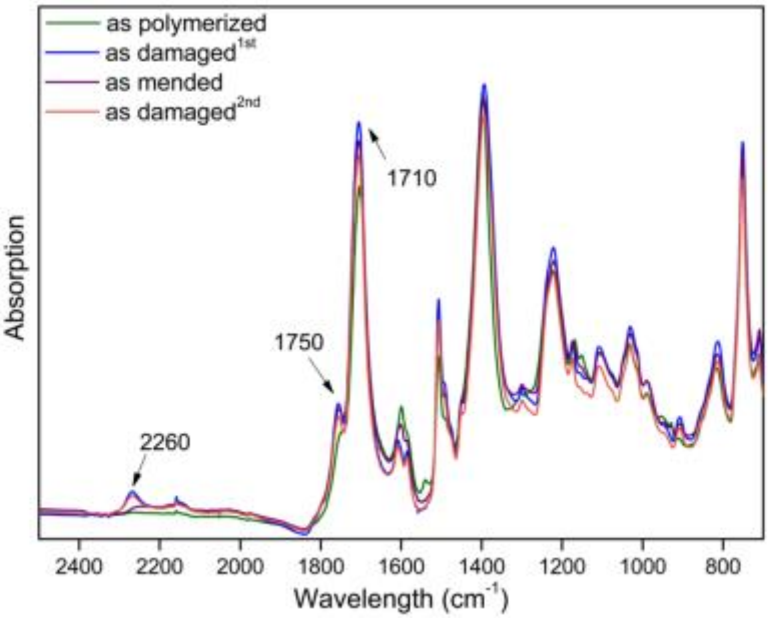

Figure 14. IR spectrum of specimens before and after grinding and following healing.

3.4 Thermal Analysis of 1TDI/1EPON, 1.5TDI/1EPON and 2TDI/1Epon polymers

Lastly, in order to demonstrate the superior thermal stability of ISOX polymers, specimens were examined by dynamic mechanical analysis (DMA) and thermogravimetric analysis (TGA). The DMA result of 1.5TDI/1Epon is shown in Figure 15a with the T_g values for 1TDI/1Epon, 1.5TDI/1Epon, and 2TDI/1Epon identified as 205ºC, 258ºC, and 281ºC, respectively. A higher T_g was obtained for the higher proportion of isocyanates in the original mixture because of higher density of isocyanurate rings in the network. The high service temperature ranging from 205ºC to 281ºC, is comparable with aromatic polyamide, which is well known as a high-temperature specialty polymer with upper service temperature ranging from 197ºC to 247ºC. The onset decomposition temperature (T_d) is another important parameter to determine the thermal stability of polymer materials. T_d is defined as the temperature at 5% weight loss of the sample as measured from TGA testing as shown in Figure 15b. The measured values of T_d for 1TDI/1Epon, 1.5TDI/1Epon and 2TDI/1Epon were 371ºC, 381ºC, and 390ºC, respectively. The T_d increases with higher proportion of isocyanates in original mixture. Similar to the DMA results, this trend is due to the increasing cross link density. These results reveal the high-temperature-resistance nature of the ISOX polymers.

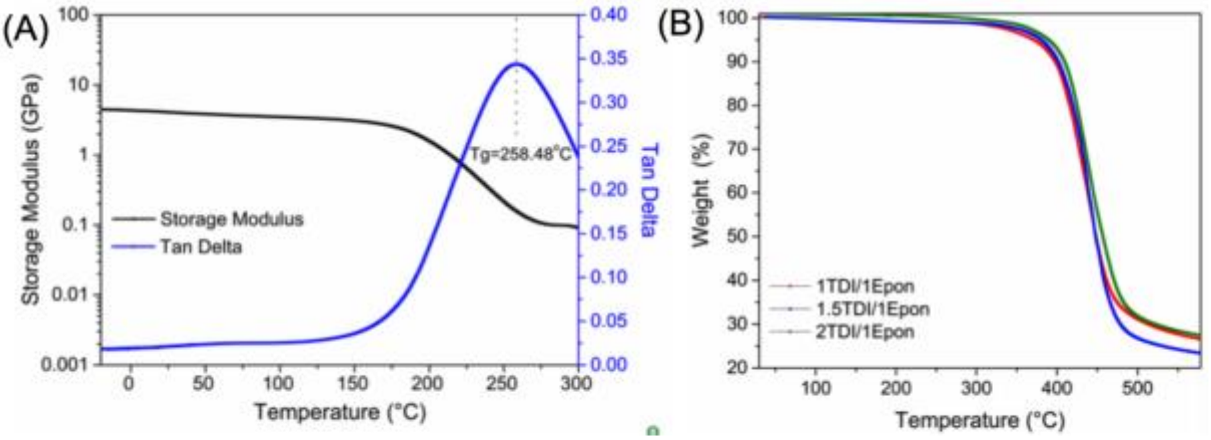

Figure 15. (A) DMA result of 1.5TDI/1Epon as an example (B) TGA result of 1TDI/1Epon,1.5TDI/1Epon and 2TDI/1Epon.

Table 1. Comparison of mechanical properties between ISOX polymers (ambient conditions/ at 125°C), self-healing polyurethane based on DA reaction, and commonly used epoxy.

Properties	1TDI/1DGEBF (SD)	1.5TDI/1DGEBF (SD)	2TDI/1DGEBF (SD)	DA Polymers[14] (SD)	Commonly Used Epoxy
Ultimate tensile strength ~25°C (MPa)	74.84(9.74)/	84.43(14.47)/	76.06(4.48)/	87.8(7.6)/ -[a]	35-130[21]/ 21.55(0.55)[40]
125°C (MPa)		60.13 (4.89)			
Ultimate tensile strain at ~25°C/125°C (%)	2.23(0.47)/	2.22(0.62)/ 2.98(0.46)	2.07(0.39)/	5.4(2.8)/ -[a]	2-6[21]/ 13.63(0.29)[40]
Young's modulus at ~25°C/125°C (GPa)	4.11(0.11)/	4.47(0.16)/ 2.51(0.05)	4.40 (0.13)/	2.57(0.17)/ -[a]	4.5[21]/ 1.52(0.17)[40]
T_g (°C)	187	252	270	45.6	180[24]
T_d (°C)	365.4(1.2)	363.1(3.7)	359.9(2.8)	130	343[41]

[a] data not available

5.0 Conclusion

This project has demonstrated engineering polymers with high strength and stiffness that exhibit self-healing behavior and thermal stability beyond any previously developed material. The effort has demonstrated the use of both the DA reaction between Furfural Alcohol and maleimide as well as anthracene and maleimide moieties to achieve high self-healing efficiency, yielding polymers and composites that exhibit no thermal degradation below 240 °C. The self-healing behavior is obtained through the reformation of mechanically cleaved DA adducts rather than thermally reversible DA reactions which place limits on the polymer's use temperature. High temperature stable self-healing polyurethanes were synthesized and showed high average first healing efficiencies up to 94%. The developed monomers were entirely liquid and thus, the self-healing CFRP composites could be also fabricated through resin transfer molding.

Furthermore, this work has demonstrated a new self-mending mechanism based on the mechano-chemical cycloreversion of isocyanurate rings. It has been shown that fracture leads to a scission of the isocyanurate rings, leaving reactive isocyanates that can re-trimerize to mend the crack. Isocyanurates are widely known to yield high thermal stability and thus endow the self-mendable polymer with a T_g of 270°C, which is the highest reported value for an intrinsically healing thermoset polymer. The cycloreversion of the isocyanurate rings to free isocyanates was confirmed through IR-spectrometry, and self-mending studies of compact tension specimens showed a first mending efficiency of 50.98%. Fracture toughness of the polymers recovered after thermal annealing due to the recovery of the high-density mechano-responsive isocyanurate rings, which act as cross-links in the network. The remendable isocyanurate ring provides a new and promising mechano-responsive bond for designing polymer materials with both intrinsic self-mending and high service temperature.

6.0 References

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