High Service Temperature, Self-Mendable Thermosets Networked by Isocyanurate Rings

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Abstract

A new mending chemistry exhibiting stability at extreme temperatures and holding mechanical properties as well as mechanical stability comparable to widely used engineering plastics is reported here. This mendable thermoset polymer is synthesized using commodity reactants through the formation of a 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. After mechanically initiated cycloreversion, the recovery of isocyanurate rings in a solid state is thermally initiated. This research is the first demonstration of an isocyanurate ring as a repairing moiety. We developed a new class of intrinsic self-mendable polymers withstanding high temperatures, which will greatly impact the application of thermoset polymers in the field of structural laminates and electronics packaging.

Keywords: self-mendable thermoset; isocyanurate cross-links; high T_g .

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 capsules³ 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 mercaptan⁹ and dicyclopentadiene.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 quick 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 agents.

The second mechanism is called intrinsic healing, which is based on a reversible chemical reaction. Reversible Diels–Alder (DA) reactions between for example, furan (F) and maleimide (M)^{11,12} or anthracene (A) and M¹³⁻¹⁵ have been broadly studied and demonstrated to hold great potential for self-healing. Wudl et.al¹¹ 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 Sodano¹⁴ 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 self-healing polymer materials, intrinsic self-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, leading to 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, anthracene 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} the use of thermal cleaving to assist in healing is limited when the cleaving temperature of A-M DA adducts is beyond the decomposition temperature of the polymers. For this reason, 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 .¹⁸ Thus, the development of self-healing polymers which

exhibit a higher T_g is needed such that they can be used at 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.al¹⁹ reported a self-healing gel by incorporating reshuffling trithiocarbonate units in a flexible poly (n-butyl acrylate) matrix, where 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.²⁰ 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

Three isocyanurate-oxazolidone (ISOX)²²⁻²⁴ polymers, referred to 1TDI/1DGEBF, 1.5TDI/1DGEBF and 2TDI/1DGEBF (TDI represents tolylene-2, 4-diisocyanate and diglycidylether of bisphenol F is abbreviated as DGEBF), are synthesized to study the new mending chemistry; and trimers of isocyanates, termed isocyanurate rings, shown as the 6-member-rings in Fig. 1 (A), are believed to be mechano-responsive bonds. Isocyanurate rings are embedded with increasing density for 1TDI/1DGEBF, 1.5TDI/1DGEBF and 2TDI/1DGEBF in the network with the T_d reaching 365°C and the T_g reaching 270°C. To the best of the authors' knowledge, this work is the first to show an isocyanurate ring as a repairing moiety. The mending concept derives from the cycloreversion of isocyanurate rings predominated under mechanical stress in a solid state. This deformation generates free isocyanates at the crack face, which trimerize under thermal stimulus to reform the polymer network across the crack and return strength to the polymer. Due to the brittle nature of isocyanurate rings,²² DGEBF was introduced to produce oxazolidone, shown as the 5-member-ring in Fig. 1 (A), as a chain extender in the network, which imparts improved toughness to the polymers. The reversibility of isocyanurate ring formation was reported to take place at very high temperature, approximately 300°C, by thermal dissociation of isocyanurate rings to isocyanates.²⁵⁻²⁸ Due to the extreme

temperature where thermal reversibility is expected, the mechano-reversibility of the isocyanurates is necessary to induce healing in isocyanurate-rich polymers. Many studies have reported similar reversibility that utilized mechano-responsive polymers.²⁹ Marx et al.³⁰ used a constant external force to open the benzocyclobutene cores as the mechanophores in the polyethylene-like oligomers. FT-IR was used to confirmed the reversion of cyclobutane to the original cinnamoyl structure from grinding 1,1,1-tris-(cinnamoyloxymethyl) ethane (TCE) polymers.³¹ Oya et al.¹⁴ proved the mechano-chemical reversibility of A-M DA adducts by UV/vis spectroscopy. Chung et al.³² verified mechanical damage and thermal repair of perfluorocyclobutane (PFCB) groups by ATR-IR, and Craig et al.³³ utilized ¹⁹F-NMR to further confirm this mechano-chemical reversibility. Our work shows that the isocyanurate rings are dissociated by mechanical stress to generate free isocyanates, which allows repeatable crack mending under thermal stimulus. The developed polymers presented in this work combine the highest reported thermal stability for a mendable polymer with high mending efficiency thus yielding high service temperature polymers with reformation of mechanical properties after cracking.

Fig. 1 (A) Isocyanurate rings as cross-links in the polymers. (B) Compact tension configuration.

2. Experimental

2.1 Sample Preparation

Diglycidylether of bisphenol F (DGEBF) was purchased from Momentive. Toluene-2, 4-diisocyanate (TDI) 80% tech and N, N-Dimethylbenzylamine (BDMA) 99% were purchased from Acros Organics. All the chemicals were used as received. 1TDI/1DGEBF was prepared by mixing 1 mole of TDI, 1 mole of DGEBF and 0.1wt% BDMA as catalyst; 1.5TDI/1DGEBF and 2TDI/1DGEBF were prepared in

the same way with 1.5mole TDI and 2TDI respectively. TDI and DGEBF were mixed thoroughly by a vortex mixer for 10 minutes and the mixture was degassed under vacuum for 30 minutes until no bubbles were visible before the BDMA was added, yielding a transparent liquid. The blended resin was transferred to a RTV664 silicone mold and placed in a vacuum oven under a nitrogen atmosphere. The 1TDI/1DGEBF, 1.5TDI/1DGEBF and 2TDI/1DGEBF samples were cured at 80°C for 1 h and post cure at 200°C for 20 h, with another 20 h of annealing at 200°C.

2.2 Mending Efficiency Measurement

The samples used for measuring mending efficiencies had average dimensions of 1.30 in. x 1.20 in. x 0.32 in. and a computer numerical control (CNC) mill was used to machine the samples to the specific dimensions for a compact tension (CT) specimen defined in ASTM D5045 as shown in Fig. 1 (B), although the specimen geometry was modified slightly through the addition of a resting hole along the crack path to stop the crack during uncontrolled crack growth. Uncontrolled crack growth is not wanted because it complicates measurement of the mending efficiency as perfect mating of the two fractured surfaces during mending is generally not possible leading to unnecessary variability in mending behavior. The notch length also was shortened to stop the crack at the resting hole due to the brittle nature of polyisocyanurate rings.³⁴ The fracture load was measured for the initial sample, and then mended and retested three successive times to determine the repeated mending efficiency using an Instron 5956 with a constant opening rate of 0.1mm/min under ambient conditions. The average fracture load values were obtained from six specimens, based on the general procedure of ASTM D5045.

2.3 ATR-IR, DMA, TGA Characterization and Measurement of Mechanical Properties

IR spectra were recorded over a range of 600-4000 cm^{-1} with a Nicolet iS50 spectrometer using a diamond ATR from Thermo Scientific. A TA Instruments Q800 dynamic mechanical analyzer (DMA) was used to measure the T_g of the polymers with 28mm x 6.5mm x 0.6mm samples loaded at 1Hz under tension over a temperature range from 25°C to 320°C at a heating rate of 2°C/min. A TA Instruments SDT Q600 thermogravimetric analyzer (TGA) was used to characterize the polymer's thermal stability over a temperature range from 25°C to 600°C at a heating rate of 20°C/min and a sample purge flow rate of nitrogen at 60 mL/min. The dimension of 1TDI/1DGEBF, 1.5TDI/1DGEBF and 2TDI/1DGEBF tensile testing samples was decided according to ASTM 638 Type IV. The samples were molded and prepared with the same curing procedure as CT samples. At least five flat specimens were tested for every sample to measure the ultimate tensile strength, ultimate tensile strain and Young's modulus. The samples were first tested under

ambient conditions and then at 125°C, the testing speed of 1mm/min was used in both conditions.

3. Results and Discussion

3.1 Preparation of Self-Mendable Polymers

A strong characteristic peak of the isocyanurate ring at 1760 cm^{-1} showed for the TDI/DGEBF cured samples, which were cured at 80°C, post cure at 200°C and another 20 h for annealing at 200°C in the oven. Annealing was expected to release residual stresses in the polymer and produce improved mechanical properties. ATR-IR was used to verify the curing process, with results shown in Fig. 2. For cured samples, the peak at 2260 cm^{-1} (carbonyl of isocyanate) completely disappears, compared with the TDI/DGEBF mixture without the curing process which shows a strong peak at 2260 cm^{-1} . A peak at 910 cm^{-1} , which can be observed in all the samples, is attributed to the epoxide residue in the polymers. New peaks appear at 1710 cm^{-1} (carbonyl of oxazolidone), 1760 cm^{-1} (carbonyl of isocyanurate) and 1100 cm^{-1} (C-O-C of ether) are observed in all TDI/DGEBF cured samples. This change in spectra confirmed the formation of the polymer network via trimerization of isocyanates to isocyanurate rings, the formation of oxazolidone as chain extenders by reaction of DGEBF with isocyanurate rings, and the formation of ether through homopolymerization of DGEBF.³⁵

Fig. 2 ATR-IR spectra of TDI/DGEBF mixture without curing process, 1TDI/1DGEBF, 1.5TDI/1DGEBF and 2TDI/1DGEBF cured samples.

3.2 Mending Efficiency

The mending performance of 1TDI/1DGEBF, 1.5TDI/1DGEBF and 2TDI/1DGEBF were evaluated through compact tension (CT) tests. The maximum load to induce fracture in the original samples and the three successively healed 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/1DGEBF samples were 43.52%, 31.63% and 26.49%, respectively; for 1.5TDI/1DGEBF samples, they were 49.33%, 33.38%, and 32.55%, respectively; for 2TDI/1DGEBF samples, they were 50.98%, 42.00%, and 42.85% respectively, with the error bars representing the standard deviation shown in Fig. 3 (A).

$$\text{Mending Efficiency (\%)} = 100 \times \frac{\text{Maximum Load of Mended Sample}}{\text{Maximum Load of Original Sample}} \quad (1)$$

Fig.3 (A) Average mending Efficiencies of 1TDI/1DGEBF, 1.5TDI/1DGEBF and 2TDI/1DGEBF for the first, second and third mending treatment. (B) Comparison of fractured sample and mended sample. (C)-(E) Examples of failure load plot for 1TDI/1 DGEBF, 1.5TDI/1 DGEBF, and 2TDI/1 DGEBF, respectively.

Two possible explanations for why the mending efficiencies of these samples could not reach 100% exist. One explanation is that the rupture of bonds induced by external mechanical stress is not 100% isocyanurate rings. Large external stress

leads to the unselective scission of covalent bonds in the network, resulting in the presence of a crack shown in Fig. 3 (B). Other bonds such as N-C bonds that connect isocyanurate rings to the benzene rings could be ruptured upon fracture. Thus, irreversible bond breakages may partially account for the loss in mending efficiency. The second explanation is that after the first time a specimen is fractured, the crack in the specimen becomes sharper after each healing; thus, a higher stress concentration exists in the specimen. Due to this factor, the subsequent mending samples cannot reach the original maximum load even with 100% healing. It is notable that the mending efficiency between fractured specimens is high with the mending efficiency being 73%, 68% and 82% for 1TDI/1DGEBF, 1.5TDI/1DGEBF, and 2TDI/1DGEBF, respectively, when comparing the first mending round and the second one.

3.3 Self-Mending Mechanism

In ISOX polymers, the scission of covalent bonds, rather than intermolecular slippage or damage of Van der Waals forces, occurs upon cracking. Due to the mechano-responsive nature, the dissociated isocyanurate rings under mechanical chain scission at the crack surface, are expected to trimerize again at elevated temperature. Efficient mending then can be achieved because the broken bonds are reformed upon the application of heat and pressure. Beyond reversible trimerization, additional forces are needed to fully observe the mending performance because it would bring the two crack surfaces into intimate contact so that the steric limitations can be overcome as illustrated in Fig .4. Fractured samples were mended at 200°C instead of 80°C, to accelerate the trimerization of isocyanates at the crack surface because of the lower steric effects at a higher temperature close to the polymer's T_g s.

Fig. 4 Proposed mending concept of ISOX polymers.

During the first step of the curing process at 80° C, trimerization of isocyanates is believed to be the only reaction taking place.³⁵ Part of these 6-member-rings react

with epoxide and produce 5-member-rings at higher temperature during the 200°C post cure, with the remaining 6-member-rings act as cross-links in the network.³⁵ Moller et.al³⁶ studied the fracture nucleation in cross-linked epoxy networks through an analysis of dihedral angle activity, and the result showed that bond scission took place after significant plastic strain, principally at cross-link sites, and between phenyl rings in the bisphenol moiety over short strain intervals. Their theory was also confirmed through physical experiments performed by other researchers.³⁷ Moller's simulation result supports the proposed concept that cycloreversion of isocyanurate rings takes place upon fracture under large mechanical stress. Also, possible scission between phenyl rings in the bisphenol moiety in the ISOX polymers, according to this simulation, can account for the irreversible bond scission mentioned in section 3.2, resulting in a mending efficiency less than 100%. Given the fact that tolylene-2,4-diisocyanate owning benzene ring connected to two isocyanate functional groups at the 2 and 4 positions was used, the space around isocyanurate cross-links is crowded due to the 3 benzene rings surrounding a single bulky 6-member-ring with pendant ketones. When large mechanical stress is applied, these rings are believed to be ruptured firstly because they have much less space to relax stress compared to homopolymerized epoxy chains. Secondly, isocyanurate rings are also more prone to dissociate compared to benzene rings because benzene rings are more stable with the homogeneity of carbon atoms.

According to this concept shown in Fig. 4, greater density of isocyanurate rings in the bulk sample would yield more cleavage of isocyanurate rings under external mechanical stress. This assumption indicates more isocyanates at the crack surface; and thus, more bonds at the fracture surface can be reformed and higher mending efficiency would be obtained. This is primarily proved by the increasing first healing efficiency from 43.52% for 1TDI/1DGEBF to 49.33% and 50.98% for 1.5TDI/1DGEBF and 2TDI/1DGEBF, respectively, with increasing density of isocyanurate rings. Samples with further increase in the molar fraction of diisocyanate as reactants are expected to have increasing mending efficiencies; however, they are not prepared here since the 2TDI/1DGEBF sample has a high cross-link density and stalling the crack is already difficult due to its brittleness. This brittleness can explain why the 2TDI/1DGEBF sample shows much lower failure load and extension compared to 1TDI/1DGEBF and 1.5TDI/1DGEBF samples which have a lower cross-link density, as can be seen Fig.3. The molecular weight (M_c) between cross-links is calculated following Kessler et.al.³⁸ to characterize the cross-link density of the polymers (details in Supplementary Material), with M_c of 1713g/mol, 242g/mol and 79g/mol, respectively for 1TDI/1DGEBF, 1.5TDI/1DGEBF and 2TDI/1DGEBF.

The proposed mending mechanism has been verified by analyzing the constitution of the polymer's fractured surface, and subsequently the ground polymers through ATR-IR spectra. The fractured surface of a 2TDI/1DGEBF sample was first analyzed by ATR-IR to study the chemistry of the polymer's surface and identify the presence of reactive functional groups that yield mending. 2TDI/1DGEBF was used due to its highest density of isocyanurate rings in the polymer network. In order to perform ATR-IR, the CT specimens were fractured completely without a resting hole; however, prior to each mending procedure, the IR spectrum of the fractured face was collected as shown in Fig. 5. In the IR-spectrum in Fig. 5, the isocyanate peak at 2260cm^{-1} can be observed in every fracture surface created after first, second, third fracture respectively, but not in the bulk surface before fracture of the specimen. In comparison, a second 2TDI/1DGEBF sample as a reference was prepared with the same method and it was also fractured completely through the sample; however, the fractured sample was then placed in the oven under a nitrogen atmosphere at 80°C for 1 h and subsequently annealed at 200°C for 20 h before the two separate pieces of the same CT specimen were put together under pressure and the same mending procedure was applied. After the mending treatment, the visual presence of a crack in the sample was obvious, and the sample showed little to no recovery of the mechanical

Fig. 5 (A) ATR-IR spectra of surfaces for 2TDI/1DGEBF sample in comparison with reference sample after heat treatment in the oven. (B) Enlarged view of the boxed region as seen in (A).

properties. The IR spectroscopy of the reference sample's crack surface, before the sample was placed on the hot press under pressure for mending purpose, but after the heat treatment in the oven, has no isocyanate peak, as shown in Fig. 5. The absence of mending performance for this reference sample can be explained by the fact that heat treatment leads to the reaction of free isocyanates leaving no reactive functional groups across the crack surface. This observation also eliminates the possibility that diffusion and entanglement of the polymer across the crack surface as the mending mechanism.

To further demonstrate that cleavage of the isocyanurate ring and re-trimerization of the isocyanate is responsible for the mending performance, the 2TDI/1DGEBF network polymers were pulverized and subsequently analyzed through ATR-IR spectroscopy. A small piece of bulk 2TDI/1DGEBF was initially pulverized through impact and subsequently ground into fine powder in a mortar pestle for 30 min which creates a high density of fractured surfaces allowing the IR-spectrum to be used to identify the structural change with greater fidelity. The IR-Spectrum after grinding and subsequent mending is shown in Fig. 6 with the ground material showing a characteristic isocyanates peak at 2260cm^{-1} while the bulk specimen prior to grinding shows no apparent isocyanate peak. The ground sample was then placed in the oven under nitrogen atmosphere at 80°C for 1 h, and then annealed 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 loose powder to an aggregated mass and was then tested with ATR-IR spectroscopy showing the isocyanate peak at 2260cm^{-1} completely disappears following the annealing step. 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 isocyanate peak at 2260cm^{-1} being repeatable. This repeatable cycle indicates that the free isocyanates at the crack face originate from the mechano-chemical cycloreversion of isocyanurate rings. The mechano-reversibility of this mechanical degradation contributes to the mending process including the disappearance of the crack and the recovered strength of the polymers shown in Fig. 3 (A) and (B)

Fig. 6 (A) ATR-IR spectra of powderized 2TDI/1DGEBF sample. (B) Enlarged view of the boxed region as seen in (A).

3.4 Thermal Analysis and Mechanical Properties of ISOX Polymers

In order to demonstrate the superior thermal stability of self-mendable ISOX polymers, they were examined by dynamic mechanical analysis (DMA) and thermogravimetric analysis (TGA), with the T_g and T_d shown in Table 1. The results of 1.5TDI/1DGEBF sample are shown as an example in Fig. 7(A), and the results of 1TDI/1DGEBF and 2TDI/1DGEBF samples are shown in Supplementary Material. The obtained T_g values for 1TDI/1DGEBF, 1.5TDI/1DGEBF, and 2TDI/1DGEBF are 187°C, 252°C, and 270°C respectively, with a higher T_g obtained for a higher density of isocyanurate rings in the network. This increase in T_g verified the proposed concept that an increasing 6-member ring density leads to a higher mending efficiency. The T_g s of ISOX polymers are much higher than the existing self-healing polymers based on A-M DA adducts, and the high service temperature ranging from 187°C to 270°C of the ISOX polymers is comparable with aromatic polyamide, which is well known as a high-temperature specialty polymer with upper service temperature ranging from 197°C to 247°C.³⁹ The decomposition onset temperature (T_d) as another important parameter to determine the thermal stability of polymer materials, is defined as the temperature at 5% weight loss of the sample from TGA tests. The measured values of T_d for 1TDI/1DGEBF, 1.5TDI/1DGEBF and 2TDI/1DGEBF are 365.4°C, 363.1°C, and 359.9°C respectively, which reveals the high-temperature-resistant nature of the ISOX polymers. The T_d of ISOX polymers increases with a higher proportion of oxazolidones which are believed to own higher thermal stability compared to isocyanurates,³² while the char formation increases with higher proportion of isocyanurates, as shown in Fig.7 (B).

Fig. 7 (A) DMA result of 1.5TDI/1DGEBF sample as an example. (B) TGA results of 1TDI/1DGEBF, 1.5TDI/1DGEBF and 2TDI/1DGEBF samples.

Lastly, the mechanical properties of each self-mendable polymer was investigated through tensile testing, with average values of ultimate tensile strength, ultimate tensile strain and Young's modulus calculated with standard deviation listed in the bracket in Table 1. Under ambient conditions, the tensile strength of ISOX

polymers is close to the reported tensile strength (as shown in Table 1) of intrinsic self-healing polyurethane based on F-M DA adducts,¹⁴ while three ISOX polymers show superior Young's modulus compared to these prior materials.^{14,15} Furthermore, the tensile strength, tensile strain to failure and Young's modulus of ISOX polymers are within the range of those reported for composite grade epoxy²¹, indicating the potential for these ISOX polymers as a self-healing replacement to thermoset epoxies. At 125°C where self-healing polymers based on F-M DA adducts are no longer stable nor useful, the ISOX polymers demonstrate their good mechanical stability, with the highest Young's modulus of 3GPa and tensile strength of 65MPa, as shown in Table 1.

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 Polyure- thans ¹⁴ (SD)	Commonly Used Epoxy
Ultimate tensile strength	74.84(9.74)/	84.43(14.47)/	76.06(4.48)/	87.8(7.6)/	35-130 ²¹ /
at ~25°C /125°C (MPa)	35.52(2.55)	60.13 (4.89)	65.37(5.52)	- ^a	21.55(0.55) ⁴⁰
Ultimate tensile strain at	2.23(0.47)/	2.22(0.62)/	2.07(0.39)/	5.4(2.8)/	2-6 ²¹ /
~25°C/125°C (%)	3.60(0.27)	2.98(0.46)	2.61(0.38)	- ^a	13.63(0.29) ⁴⁰
Young's modulus at	4.11(0.11)/	4.47(0.16)/	4.40 (0.13)/	2.57(0.17)/	4.5 ²¹ /
~25°C/125°C (GPa)	2.01(0.14)	2.51(0.05)	3.07(0.06)	- ^a	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

4. Conclusions

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. Lastly, the ISOX polymers utilizing this new chemistry own

superior mechanical properties and mechanical stability comparable to composite grade epoxies.²¹

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