Towards improved dual network, disulfide based, self-healing thermosets for fibre reinforced composites

SATYA AMMU

Master of Science Thesis

TU Delft

Novel Aerospace Materials

Towards improved dual network, disulfide based, self-healing thermosets for fiber reinforced composites

Thesis report

by

Satya Ammu

in partial fulfillment of the requirements for the degree of

Master of Science

in Aerospace Engineering

at the Delft University of Technology,

to be defended on Monday, August 20, 2018

Student Number:	4619196	
Thesis committee:	Dr. Santiago J. Garcia	TU Delft, Associate Professor, NovAM, Thesis supervisor
	Prof.dr.ir. Sybrand van der Zwaag	TU Delft, Professor, NovAM, Chairholder of NovAM
	Dr. Otto Bergsma	TU Delft, Assistant Professor, SIC External examiner

This page is intentionally left blank.

Acknowledgment

This thesis was performed in partial fulfillment of the requirement for Masters of Science in Aerospace Structures and Materials in the Department of Aerospace Engineering at TU Delft, Netherlands. The thesis project was carried out from Oct 1, 2017, to Aug 1, 2018, at the Novel Aerospace Materials group of the Aerospace engineering department at TU Delft.

I would like to thank my supervisor, Dr. Santiago J Garcia for his continuous support throughout the thesis for exploring new concepts and ideas to tackle the problem. His technical expertise and guidance are much appreciated as it helped me during my research to keep striving to achieve my goals and to grow as a person.

I would also like to thank Prof. Sybrand van der Zwaag for his key role in the thesis. His critique and guidance have helped me take a step back and analyze the direction of the thesis and has helped me understand better the process of research.

I would like to thank Dr. Otto Bergsma for agreeing to be a part of thesis committee. I would also like to thank Dr. Marlies Nijemeisland and Dr. Johan Bijleveld who helped me with the technical and theoretical problems encountered in this project. I cannot think of a day where I haven't asked them for some help or the other to keep my research going. Further, I would like to Shanta for taking care of all the administrative work and for always offering a helping hand whenever needed. I would also like to thank all the members of the NovAM for making this one of the best experiences of my life. Finally, I would like to thank my family and friends for always supporting me in my decisions and for being there for me through thick and thin.

Satya Ammu

Delft, 14-08-18

This page is intentionally left blank.

Abstract

In order to address the need for a mechanically strong, self-healing thermosetting polymer for fiber reinforced composites, a novel dual network epoxy containing reversible disulfide bonds has been developed recently. This hybrid epoxy had the ability to heal multiple times when incorporated into fiber reinforced composites along with easy processing routes. However, one of the problems faced by this system was the instability of thiols, which were used to prevent phase separation of the components and promote healing by increasing the S-S bond content. These thiols, however, undergo side reactions which reduce the mechanical properties of the final network along with reduced long-term healing ability.

The goal of this thesis was to study the effect of eliminating thiol from this dual-network epoxy on its mechanical and healing properties and to explore the effect of CuCl2 as a catalyst in case there is a reduction in the healing efficiency. The hybrid epoxy without thiol has been synthesized and its microscopic and macroscopic reversibility have been studied using stress relaxation and mode I opening of Double Cantilever Beam (DCB) specimens respectively.

Eliminating thiol lead to an increase in Young's modulus and strength of the hybrid epoxy. The same epoxy without thiol shows higher stress relaxation than the epoxy with thiol at 80°C. Given that in a crosslinked network, the ability to relax stress depends on the reversibility of the disulfide bonds, this indicates that the disulfide bond reversibility in the epoxy without thiol does not decrease in the absence of thiol in spite of having a stronger network at room temperature. Macroscopically, however, the epoxy with thiol had higher healing efficiency compared to the epoxy without thiol which showed almost no healing.

To address the loss in healing efficiency, the effect of $CuCl_2$ *as a catalyst to promote disulfide exchange reactions was studied. Stress relaxation experiments indicated greater relaxation in the presence of* $CuCl_2$ *along with a small increase in the stiffness of the hybrid epoxy. CuCl2 can thus be used as an alternative for thiol to promote disulfide exchange reactions at higher temperatures.*

Given that there is a dearth of literature comparing thiol-disulfide reactions with disulfide exchange reactions, the effect of thiols in this systems was unclear before. From these experiments, it can be observed that in the absence of thiols, disulfide bonds undergo stress relaxation most likely using a thermally triggered radical mediated exchange mechanism. However, the polymer architecture and the amount of disulfide content plays a key role in the macroscopic healing and this could be tuned to increase both healing and mechanical properties simultaneously.

This page is intentionally left blank.

Table of Contents

List of figures

1 Introduction

The use of fiber reinforced composites for structural applications in the aerospace industry has gained a huge momentum within the past decade due to their high stiffness to weight and strength to weight ratios when compared to traditional aerospace aluminium alloys. Both Boeing 787 Dreamliner and the Airbus 350 are jetliners constructed primarily of carbon fiber reinforced composites (50% and 53% by weight respectively).

Thermosetting polymer such as epoxies are widely used as matrix material because of their excellent mechanical properties, thermal and dimensional stability and resistance to creep and chemicals. Thermosets derive these properties from a network of organic molecular chains that are permanently cross-linked with strong covalent bonds. However, this permanent network makes them brittle and unable to be re-processed or re-shaped once cured.

Microcracks in the matrix are the most common failure mode among multidirectional composites [1] and they usually go unnoticed in physical inspection. These micro-cracks in the matrix lead to crack propagation and eventually matrix failure or fiber pull out leading to the failure of the composite. This necessitates extensive and often time-consuming, non-destructive inspection that can go beyond physical inspection. Once the damage is detected, repairing composite laminates are much more difficult than aluminum alloys. Aircrafts made from aluminum generally consists of multiple aluminum panels that can be easily replaced. However aircrafts like Boeing 787 Dreamliner and the Airbus 350 [2] that consist of large barrels of CFRP that are autoclaved and then joined together which makes it difficult and uneconomical to replace entire barrels.

In these aircrafts, the usual repair method includes replacing the damaged area with patches. However, it is very important that the properties of the patch match exactly with that of the underlying ply as composites are very sensitive to thermal expansion stresses. [3] Another thing to be kept in mind is that usually these patches are either bolted or bonded and both these methods have their own disadvantages, as they add discontinuities in the system where there could be a higher chance of failure. This difficulty in repair and maintenance directly translates to high manufacturing, maintenance and repair costs. Apart from the high manufacturing and repair costs, high-performance composites also suffer from the lack of recyclability when compared to aluminum alloys. Products from resins are mainly recovered from thermolysis and solvolysis. However, these products recovered have often too little value for the process used and hence not economically viable.

All this has led a huge increase in the research of self-healing polymer materials in which the components of the material can heal minor damages from within the system, to extend the overall lifetime of the composite and minimize the need for repair. Thus, the search for a high strength, self-healing epoxy for fiber reinforced composites is a major step towards safer, more environmentally friendly and economical fiber reinforced composites that can drastically increase the rate at which composites are incorporated into aircraft. This thesis specifically aims at developing better understanding of underlying principles to create such a system.

Unlike thermoplastics which repair based on molecular inter-diffusion, healing in thermosets is more difficult due to the inherent permanent network where there is a tradeoff between the stiffness of the network and its ability to heal. Most of the research in the literature thus focus on creating methods that can introduce external or internal agents that can alter the permanent network in case of damage. Damage recovery requires the material to have local temporary flexibility such that there is a motion of the healing agent/ polymer molecules at the region of the damage without the entire structure losing its integrity [4] which is the biggest challenge in thermoset healing.

Healing in thermosets can be achieved through either extrinsic or intrinsic methods. Extrinsic methods use a stored healing agent in micro containers like capsules or fibers which are embedded into the polymer and upon damage and crack propagation, release the healing agent. However, they have multiple disadvantages, the biggest of them being the inability to heal multiple times, and the reduction in mechanical properties caused due to the inclusion of these containers into the polymer system.

Intrinsic self-healing systems, on the other hand, have the ability to heal multiple times by breaking and reforming reversible bonds which are built into the chemical structure of the polymer. These latent functionalities are triggered upon the application of a stimulus such as heat or UV light.

1.1 Covalent Adaptable networks

The most promising option for intrinsic self-healing polymers to be used in structural composites is **Covalent Adaptable Networks (CANs**) [5] that use reversible covalent bonds throughout the network of polymer. Upon application of the specific stimulus that triggers these reversible reactions, this system undergoes stress relaxation and flow leading to a topology or structure rearrangement. CANs usually have comparable mechanical properties and chemical resistance as that of thermosets arising from a crosslinked network architecture, however, they can also be reprocessed and made to alter their shape due to the reversibility of the covalent bonds present in them. This makes them very interesting as self-healing matrix materials for composites.

Covalent Adaptable Networks (CANs) were first observed in the 1940s when vulcanized rubber and other polysulfide containing polymer networks such as thiokols showed creep when subjected to a constant stress. This characteristic which is typical to thermoplastics and absent in network polymers was studied by Green and Tobolsky. They postulated that the disulfide crosslinks broke and reformed at equilibrium. Thus, the polymer could creep without undergoing any degradation [6] [7]. In the last decade, multiple reaction mechanisms like cycloaddition reactions, transesterification reactions, transacylation reactions, disulfide exchange reactions, etc. have been used to create CANs with very different relaxation and bond rearrangement behaviors.

The two most widely used chemistries to develop CANs are **Diels- Alder reactions and Disulfide exchange reactions**. Diels- Alder reaction is the most popular thermo-reversible cyclo-addition reaction that has been studied for the creation of reversible covalent networks. It involves a reversible reaction between a conjugated diene and a substituted alkene, the most common being the reaction between furan and maleimide as shown in Figure 1-1.

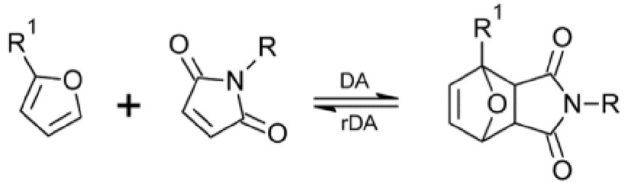


Figure 1-1 Diels-Alder reaction between furan and maleimide

It was first studied by Wudl et al [8], [9] to prepare thermally re-mendable highly crosslinked polymers using multi-furan and multi-maleimide. One of the major challenges of using DA reactions particularly in the case of epoxies is that while functionalizing the epoxy with D-A moieties, it is difficult to control undesired side reactions such as Michael addition or homopolymerization of BMI, that occur at high temperatures.[10] These side reactions form non-reversible crosslinks and reduce the healing efficiency of the polymer. Also, these polymers suffer from practical limitations arising from the use of solvents and long healing times.

To overcome this problem Turkenburg and Coope et al in 2016 [10], [11] designed a new 2 step process to create a D-A based resin intended for use in aerospace applications by minimizing the number of active components and reactive groups. The synthesis includes a two-step process shown in Figure 1-2 in which first, furfuryl amine is pre-polymerized with the diglycidyl ether of bisphenol A, DGEBA. This is then mixed with amines in the absence of maleimides at high temperatures and for a relatively long time to ensure the complete reaction of all primary and secondary amines. This is to prevent Michael addition reaction where the activated double bond of maleimide groups reacts with amines. This is them mixed with bismaleimide, BMI and extruded.

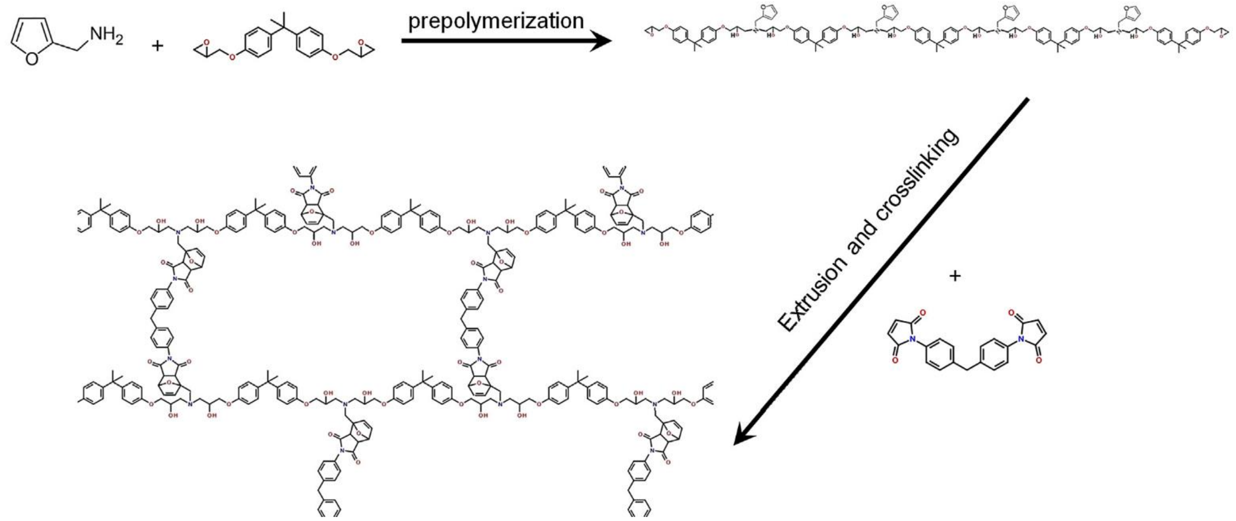


Figure 1-2: 2 step synthesis of novel DA epoxy for aerospace composites. The first step involves pre-polymerization of DGEBA with furfuryl amine followed by crosslinking with BMI [11]

Even though it yielded a relatively good epoxy network with low side reactions and had the ability to heal cracks and delamination multiple times, it still requires high-temperature healing at 150°C along with expensive monomers and a long process. Also, the polymer can only be extruded and cannot be used in methods like resin transfer infusion which is one of the most commonly used methods to produce fiber composites.

Compared to D-A reactions, **Disulfide exchange reactions** are very versatile due to the wide variety of sulfur-based chemistries that can be found. Disulfide exchange reactions ware one of the earliest studied reversible reactions due to its ubiquity in biological systems such as proteins etc.

1.2 Disulfide healing mechanisms

Disulfides undergo multiple reactions. In the presence of thiols, they undergo thiol-mediated exchange reaction. This could be either due to radical or ionic intermediates. In the absence of thiol, disulfides can either undergo dissociative homolysis reactions and/or associative metathesis and exchange reactions. The specific healing mechanism in the CAN depends on the initiation, kinetics, and yield of the above-mentioned mechanisms.

1.2.1 Thiol-mediated mechanism

Thiol-disulfide reactions are one of the most widely studied exchange reactions. It involves the deprotonation of thiols to create a thiolate ion. This thiolate ion attacks the disulfide bond and causes a nucleophilic displacement of another thiolate from the disulfide bond as shown in Figure 1-3. Even though this reaction involves the cleavage of a relatively strong S-S covalent bond (bond energy ca 60 kcal mol^{-1}) by thiolate ion and formation of a new S-S bond, it takes place at room temperature in water at neutral ph. The reaction is moderately fast (ca 10 M^{-1}min^{-1}) and has a good yield if there are no side reactions like oxidation of thiols to disulfides etc. [12]

$$
\begin{aligned}
\mathrm{RSH} &\rightleftharpoons \mathrm{RS^-} + \mathrm{H^+} \quad (\mathrm{p}K_{\mathrm{a}}{}^{\mathrm{RSH}}) \\
\mathrm{RS^-} + \mathrm{R'SSR'} &\rightleftharpoons \mathrm{RSSR'} + {}^{-}\mathrm{SR'} \\
\mathrm{H^+} + {}^{-}\mathrm{SR'} &\rightleftharpoons \mathrm{HSR'} \quad (\mathrm{p}K_{\mathrm{a}}{}^{\mathrm{R'SH}})
\end{aligned}
$$

Figure 1-3 Thiol Disulfide exchange mechanism [12]

The deprotonation reaction of thiol to create thiolate can be accelerated by raising the pH to basic conditions typically using amine base catalysts [13]. In presence of aprotic solvents like DMSO, DMF the reaction is about 1000 times faster than when compared to polar protic solvents like water. The more nucleophilic the catalyst, the easier the formation of the thiolate ion and faster the reaction. Thus, this reaction is very dependent on the presence of thiolate ions and will cease upon the protonation or removal of thiolates.

1.2.2 Thermally activated mechanisms

1.2.2.1 Disulfide Homolysis

Homolytic cleavage of disulfide bonds to give thiyl radicals as shown in Figure 1-4 has been studied in literature in the presence of UV light or high temperatures. Bond dissociation energy (BDE) for dialkyl disulfides was found to be around 65 kcal mol^{-1} in and 50 kcal mol^{-1} in diaryl disulfides. [14]

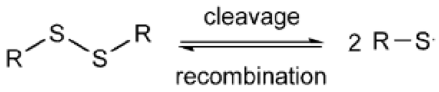


Figure 1-4 Reversible homolysis of disulfide bond

Disulfide bonds are about 40% weaker when compared to C-C bonds and are usually the weaker links in the molecule. In spite of this, on heating, *the homolysis of S-S bond takes place with very low rate constants even at 100°C.* [15] This is the reason why in most literature, *this reaction is catalyzed either with UV light or nucleophiles.* Irradiating diphenyl-disulfide at 355nm has been used to photolyze the S-S bonds and has been verified by measuring the amount of product formed as a result of disulfide homolysis and exchange. [14], [16].

Similarly, multiple experiments with nucleophiles such as triethylamine (NEt3) and tri-n-butyl phosphine (TBP) have shown to catalyze the homolysis [17]. *This is because the S-S bond is very susceptible to scission by polar reagents due to the polarizability of divalent S-S and hence is susceptible to both electrophiles and nucleophiles, but more so to nucleophiles.*

Dissociation of monosubstituted diphenyl disulfides

This study done by Ruiperez et al [18] compares various disulfide containing aromatic crosslinkers as shown in Figure 1-5 with different end groups to simulate their dissociation energy. They studied that Electron Withdrawing Groups (EWGs) CO-CH_3 increase both the spin density and the bond dissociation energy (BDE). Phenyl rings substituted with Electron Donating Groups (EDGs) like NH_2 reduce the bond dissociation energy as shown in Figure 1-6. These EDGs activate the phenyl ring by delocalizing the unpaired electron of the generated sulfenyl radical into the aromatic ring. Disulfide crosslinkers with phenyl groups that are para- substituted with electron donating groups like NH_2 hence readily dissociate into radicals at room temperature.

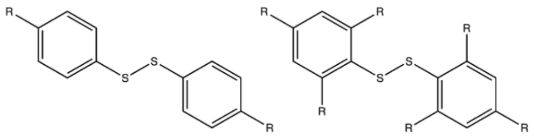
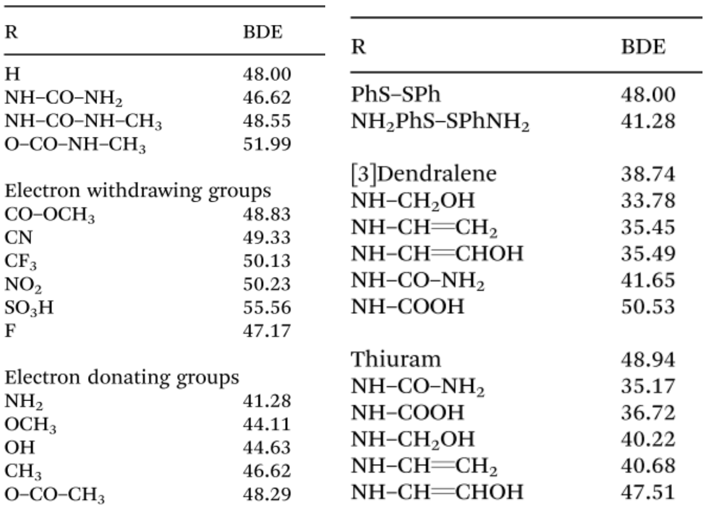


Figure 1-5 Model diphenyl disulfide compounds used in the analysis of the S–S bond cleavage by Ruiperez et al [18]



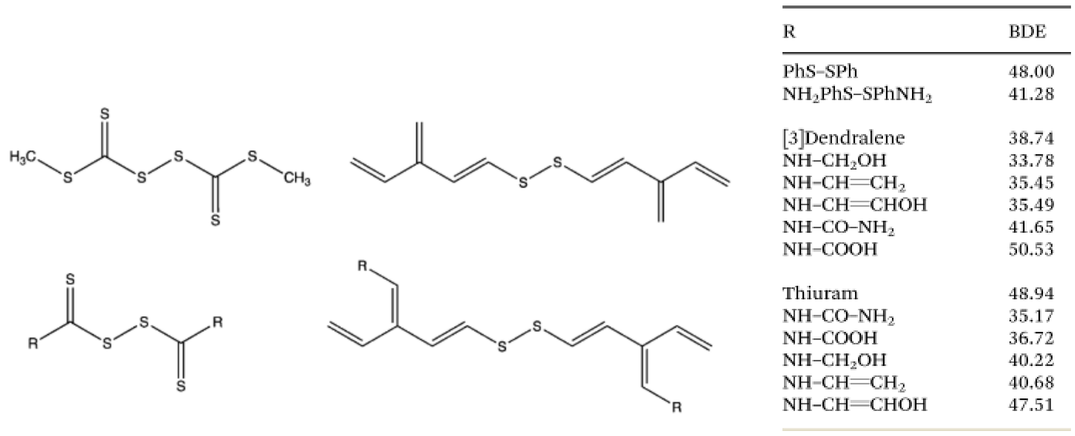
R	BDE
H	48.00
NH–CO–NH_2	46.62
NH–CO–NH–CH_3	48.55
O–CO–NH–CH_3	51.99
Electron withdrawing groups	
CO–OCH_3	48.83
CN	49.33
CF_3	50.13
NO_2	50.23
SO_3H	55.56
F	47.17
Electron donating groups	
NH_2	41.28
OCH_3	44.11
OH	44.63
CH_3	46.62
O–CO–CH_3	48.29

R	BDE
PhS–SPh	48.00
NH_2PhS–SPhNH_2	41.28
[3]Dendralene	38.74
NH–CH_2OH	33.78
NH–CH=CH_2	35.45
NH–CH=CHOH	35.49
NH–CO–NH_2	41.65
NH–COOH	50.53
Thiuram	48.94
NH–CO–NH_2	35.17
NH–COOH	36.72
NH–CH_2OH	40.22
NH–CH=CH_2	40.68
NH–CH=CHOH	47.51

Figure 1-6 Influence of end groups on the bond dissociation energy of disulfides (in kcal mol-1) in an aromatic disulfide crosslinker [18]

Dissociation of non-aromatic conjugated disulfides

To study the same effect of delocalization and conjugation in the aromatic ring in non-aromatic disulfides, Ruiperez et al [18] chose conjugated disulfides such as dendralene and thiuram disulfides as shown in Figure 1-7. These show lower bond dissociation energies than that of the para-substituted amine derivatives and close to the trisubstituted ones. Thus it is easier to cleave them which makes them good candidates for self-healing materials.[18]



R	BDE
PhS–SPh	48.00
NH_2PhS–SPhNH_2	41.28
[3]Dendralene	38.74
NH–CH_2OH	33.78
NH–CH=CH_2	35.45
NH–CH=CHOH	35.49
NH–CO–NH_2	41.65
NH–COOH	50.53
Thiuram	48.94
NH–CO–NH_2	35.17
NH–COOH	36.72
NH–CH_2OH	40.22
NH–CH=CH_2	40.68
NH–CH=CHOH	47.51

Figure 1-7 Molecular structures of thiuram (top left) and [3]dendralene disulfides (top right), and the corresponding derivatives (bottom) along with their BDE

Though radical formation from aromatic disulfides and conjugated non-aromatic disulfides has been studied in much detail, there is relatively very less information about aliphatic disulfides.

1.2.2.2 Radical-mediated disulfide metathesis and exchange

Disulfide exchange reaction is a more complex reaction in the literature that could have two possible reaction mechanisms:

i) [2+2] disulfide metathesis:

This mechanism was initially proposed by Odriozola et al [19] in their work on self-healing elastomers based on disulfide bonds and further explored by Ruipérez et al [18]. This mechanism involves two disulfide bonds forming a temporary, 4- membered ring before splitting to create two separate disulfide bonds with their chains exchanged as shown in Figure 1-8. This reaction doesn't require a radical or an ion to initiate the reaction and only requires suitable temperature or photo-excitation to initiate the bond formation and bond breaking.

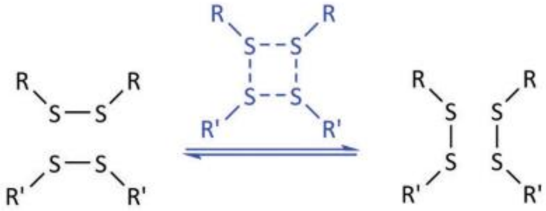


Figure 1-8 Schematic representation of the [2+2] metathesis mechanism by Asua et al [16]

Ruipérez et. al [18] used quantum chemical calculations to study both the metathesis and disulfide exchange reaction. They found no computational evidence for the 4 membered transition state structures that occur during the metathesis reaction.

Similarly research done by Asua et al [16] showed that this is not a very likely reaction mechanism. *Thus, it is most likely that the disulfide exchange doesn't take place through the [2+2] metathesis, but rather the [2+1] radical mediated reaction*.

ii) [2+1] radical-mediated mechanism:

Hernandez et al used in 2016 [20] to Electron Spin Resonance (ESR) Spectroscopy observe the creation of radicals in di/ polysulfides. In the same year, Asua et al [16] studied the exchange reaction between 4-aminophenyl disulfide and diphenyl disulfide. In the presence of a radical scavenger TEMPO, the exchange reaction was completely inhibited which showed that the reaction mechanism is radical mediated. Further, exposure to UV light the rate of reaction increased rapidly. Both these work supports the computations done by Ruipérez et. Al in 2014 to show that disulfide exchange reaction is mostly carried on by radical-mediated 2+1 exchange reaction [18].

The 2+1 radical-mediated mechanism involves the homolytic cleavage of an S-S bond to create thiyl radicals. These thiyl radicals attack the disulfide bond and create a 3 membered structure which splits again to create a new disulfide bond along with another thiyl radical as shown in Figure 1-9. Thus, this reaction involves two parts*: a dissociative reaction which creates the thiyl radicals and an associative reaction where the thiyl radicals first create a new bond with the disulfide bonds and then break an old bond*. It is usually considered as an associative reaction in the presence of a catalyst and follows the characteristics of an associative reaction.

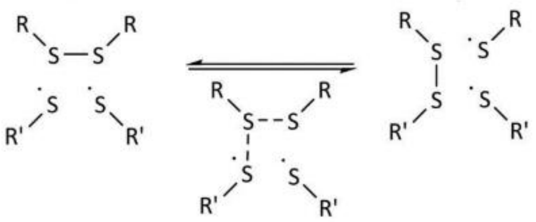
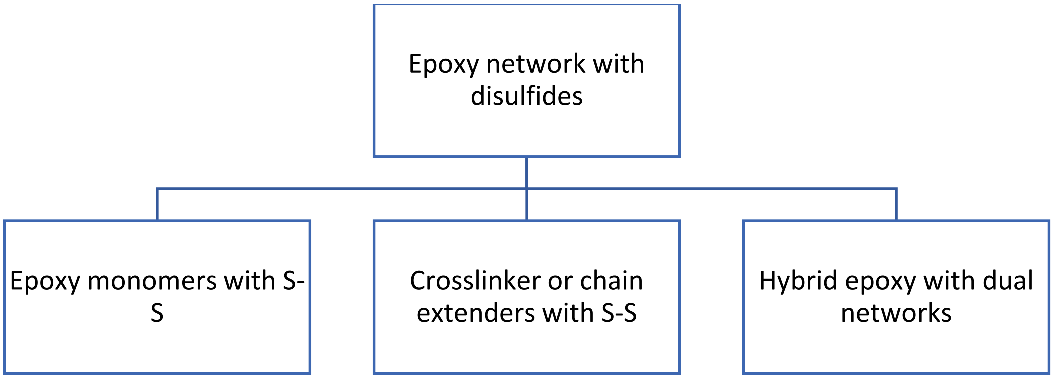


Figure 1-9 Schematic representation of [2+1] radical-mediated mechanism [16].

Literature, thus, shows that among the exchange reactions, the most likely mechanism of disulfide exchange is 2+1 radical-mediated mechanism. Multiple papers have found theoretical and experimental proof to the hypothesis that this is the governing mechanism in the absence of thiols. The 2+1 mechanism involves both homolysis to create radicals followed by radical exchange reaction. However, the kinetics of homolysis vs radical exchange from non-aromatic disulfides such as BDS especially when present in a network containing epoxy groups is largely unexplored. This remains one of the biggest gaps in literature: the comparison between the kinetics of these two mechanisms, especially in epoxy-amine systems.

1.3 Dual network disulfide-based epoxies

As mentioned before, disulfide scission and exchange in polymers was first observed by Tobolsky et al in 1964. Even though this knowledge was known more than 50 years ago, disulfide exchange was mostly considered an unwanted reaction causing creep in natural rubber. Their potential for creating reversible thermosetting polymers and specifically epoxies has only gained huge momentum in the past decade. Through the past decade, various approaches have been tried to incorporate disulfides within the epoxy network. These approaches have been shown in the flow chart below. This includes modification of either the epoxy monomer to contain S-S bonds or the crosslinker to contain S-S bonds. However, there are also more approaches such as creating a hybrid epoxy with S-S bonds where the mechanical and healing properties are independently tuned.



Appendix A outlines some of the major developments in the epoxy monomers with S-S along with some cross linkers that contain S-S. However, most of these methods either have insufficient mechanical properties or require extremely high temperature and pressure to heal. Similarly, many of these techniques are not up scalable due to the prohibitive cost of the monomers used or the long processing techniques which are difficult to follow on a large scale.

To address this, Abdolah Zadeh et. al [21], created the first generation dual network epoxy which contains both organic and inorganic crosslinks. Using dual networks allows having a permanent epoxy amine network to control the network stiffness and toughness while having a reversible inorganic network.

This novel material uses two silicon alkoxides: Bis[3-(triethoxysilyl) propyl] tetrasulfide and (3-Aminopropyl) trimethoxysilane abbreviated as BTS and APS respectively in Figure 1-10.

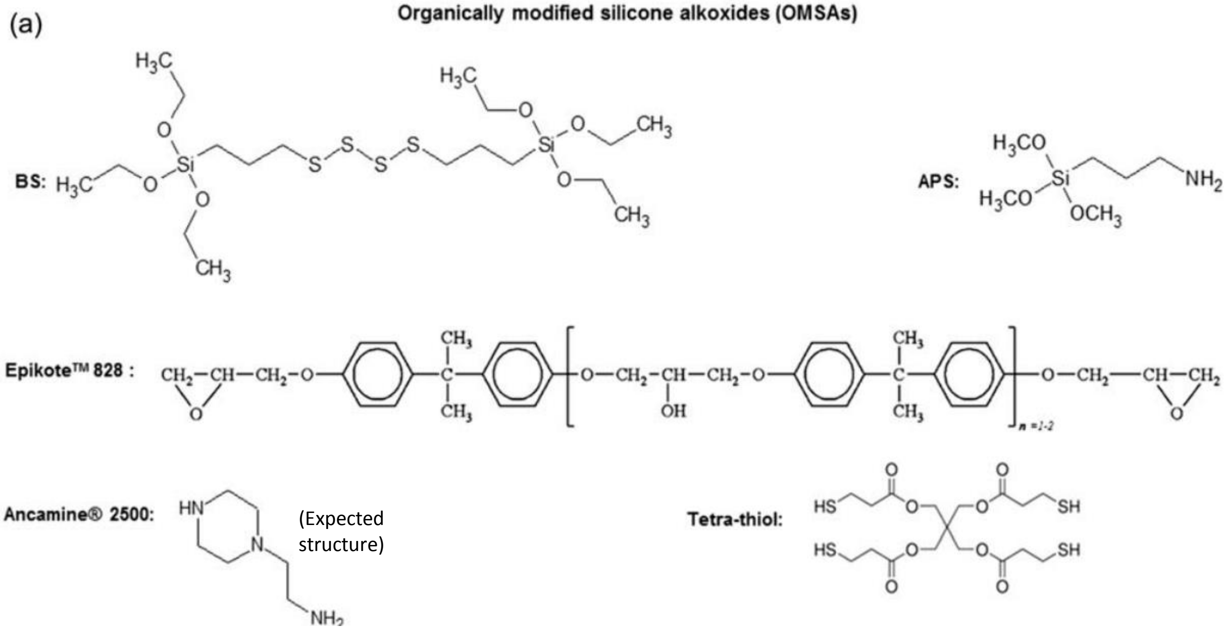


Figure 1-10: Chemical structure of Bis[3-(triethoxysilyl)propyl] tetrasulfide (BTS) and (3-Aminopropyl)trimethoxysilane (APS), Epikote and Tetrathiol. Since Ancamine is a commercial compound whose structure is unknown, this is an expected structure

These two silicon alkoxides undergo a hydrolysis and condensation reaction to create an inorganic Si-O-Si network as shown in the schematic in Figure 1-11. The hydrolysis reaction is relatively very fast in the presence in an alkaline pH. This Si-O-Si inorganic network is also modified organically by the addition of EpikoteTM 828 epoxy which links to the APS due to the presence of the epoxy-amine organic network. The idealized structure of the final network is shown in Figure 1-12.

$$SiOR + H_2O \rightarrow SiOH + ROH$$

$$SiOR + SiOH \rightarrow SiOSi + ROH$$

$$SiOH + SiOH \rightarrow SiOSi + H_2O$$

Figure 1-11 Schematic of hydrolysis and condensation reaction of silicon alkoxides

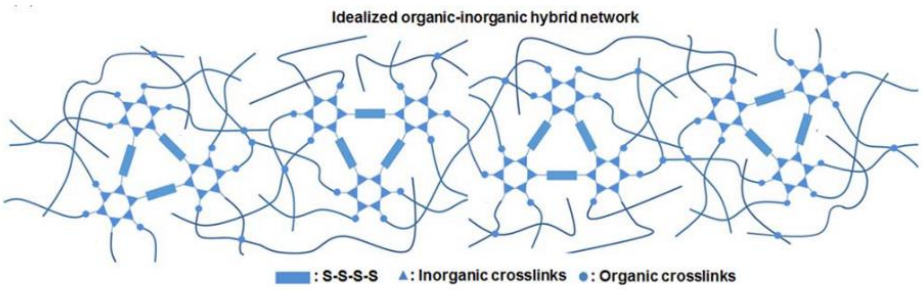


Figure 1-12 Idealized structure of the dual network [21]

The tetra-sulfide bonds [-S-S-S-S-] in BTS break and reform at higher temperatures and are responsible for the mesoscale flow and healing by interface restoration while the irreversible organic bonds maintain the mechanical integrity. The tetrathiol was added to 1) prevent any phase separation while mixing the individual components and 2) help in the tetrasulfide cleavage to create disulfide bonds and reduce release of H_2S gas. This polymer was cast and cured at 70°C for 2 hours. This paper explored the effect of varying the quantities of chemical precursors on the interfacial healing efficiency of the final polymer measured using the recovery in the tensile strength and the gap closure efficiency of the healed specimen at various temperatures.

Increase in crosslinking density in the organic network leads to higher mechanical properties but lower healing properties, and this was observed in this work, however, they also found that increasing the inorganic network with reversible bonds led to an increase in both mechanical and self-healing properties up to a point. Even though the polymer they developed in this paper had a Tg around -11°C and had low stiffness, their work prompted that there is a way to develop polymers with high strength and good healing efficiency simultaneously by using a dual network which can be independently tuned.

In 2016, Abdolah Zadeh et.al [22] studied the effect of curing time on the mechanical and healing behavior of the polymer by measuring the recovery in resistance to crack propagation during a fracture test. They observed that increasing curing times lead to an increase in mechanical properties due to a more stable network formation which in turn reduced the flow kinetics. However, contrary to popular expectation, there was no decrease in the interfacial healing ability and it remained independent of the curing degree. This behavior has been attributed to the increase in the inorganic crosslinking of the alkoxy silanes leading to a stiffer inorganic network, however, the reversible S–S bridges remain constant and hence healing efficiency is unaffected.

Following this work, Post et. al [23] modified the network to make it more suitable to be used in fiber composites by replacing the tetrasulfide inorganic precursor with disulfide precursor as shown in Figure 1-13. The disulfide precursor was more chemically stable and hence mechanically stronger than the tetrasulfide precursor. This also leads to a reduction of reaction kinetics so that it can be processed in composites using vacuum assisted resin transfer along with reduced H_2S release.

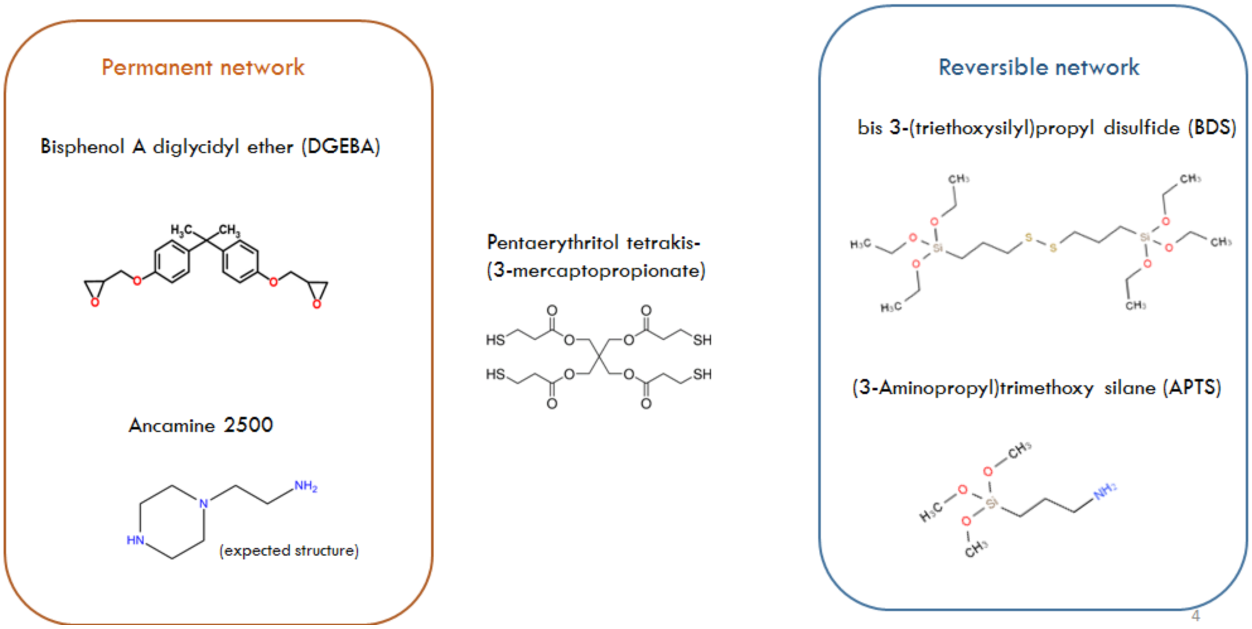


Figure 1-13 Chemical structure of components used Bis[3-(triethoxysilyl)propyl] disulfide (BDS), (3-Aminopropyl) trimethoxy silane (APS), Epikote and Tetrathiol and Ancamine

Resin component	Weight ratio
Epon TM 828	1
Ancamine®2500	0,646
(3-Aminopropyl)trimethoxysilane	0,076
Pentaerythritol tetrakis (3-mercaptopropionate)	0,579
Bis [3-(triethoxysilyl)propyl]disulfide	0,566
Triethylamine	0,014

Figure 1-14 Weight ratio of resin components in the self-healing polymer matrix

The new hybrid epoxy was cured for 60 hours at 100°C to ensure completion of the inorganic reaction. It had Young's modulus of 800-1200 MPa and multiple healing cycles at 70-85°C and could be processed by conventional composite processing techniques like vacuum infusion. It was found that small-scale damages (<cm^2) caused from low-velocity impact could be healed at 0.2 bar pressure, however large scale damages (>cm^2) required higher pressures to bring the two surfaces in contact. This work opened up the path towards the development of self-healing hybrid epoxies which can be used for aerospace composites with mechanical properties comparable to commercial epoxies.

Even though composites made from this dual network thermoset displayed high flexural modulus (10.1+-0.7GPa) and yield strength (55.0+-3.7 Moa), Post et al [23] mention that the mechanical properties are not yet at a level where they can fully compete with commercial epoxies.

2 Problem Statement

One of the main challenges while creating self-healing epoxy for aerospace composites is the balance between the mechanical properties and healing properties. The low strength of self-healing polymers when compared to the commercially available epoxies limits their widespread use. Using small rigid monomers increases the stiffness of the network and in turn the stiffness of the material. However, this directly reduces the ability of the material to undergo relaxation at high temperatures and heal.

Thus, one of the key objectives especially with thermosetting polymers for aerospace composites is to increase the stiffness and the strength of the self-healing epoxy without reducing their healing efficiency. This would push the polymer towards the target region as depicted by Post et al in Figure 2-1.

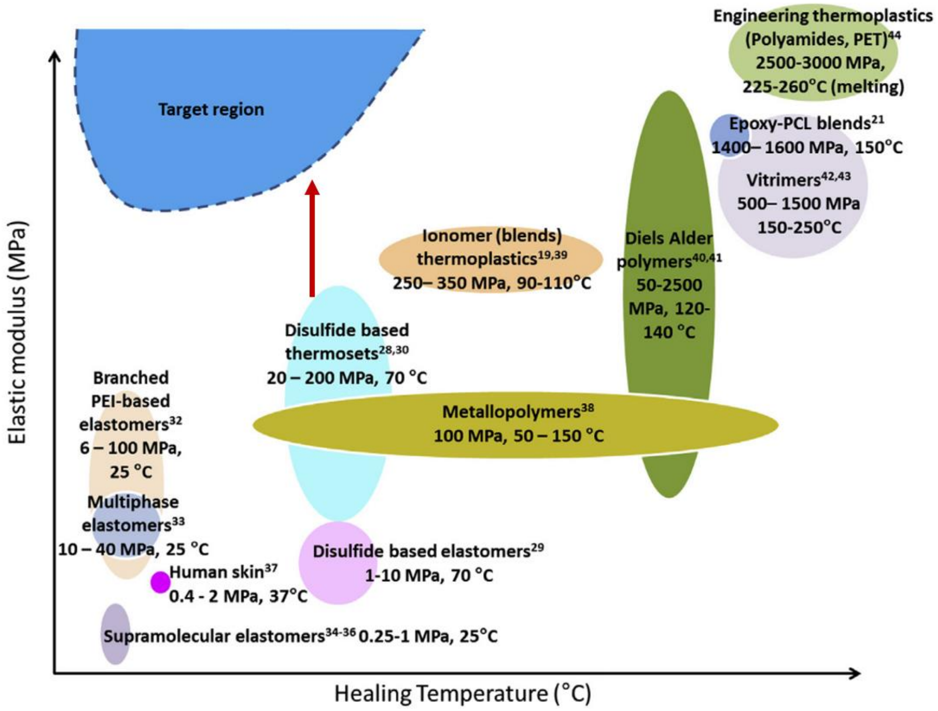


Figure 2-1 Overview of elastic modulus vs healing temperature of intrinsic self-healing polymers [23]

Since the idea behind using a dual network epoxy was to separate the two aspects into different networks such that the *inorganic network which consists of the reversible disulfides can be kept constant while the organic network can be tuned to increase the mechanical properties.* Hence, the organic network and the resulting polymer architecture was studied to improve its stiffness. *In the case there is a reduction in healing efficiency due to the increase in mechanical properties, a study of CuCl2 as a catalyst to increase healing efficiency was to be studied.*

The research plan considering the goal mentioned before is shown below in Figure 2-2. Epoxy monomers with disulfide bonds like EPS 25 and crosslinkers with S-S bonds like 4-aminophenyl disulfide were incorporated into the epoxy system as shown in Appendix A. However most of these chemicals either do not have the stiffness required for application in composites or the monomers are too expensive to be used in large-scale application. Thus, the focus of this thesis was to study the network structure of the organic network in order to increase stiffness. On studying the cured polymer through FTIR, secondary amines were observed in the cured network indicating incomplete reaction of amines.

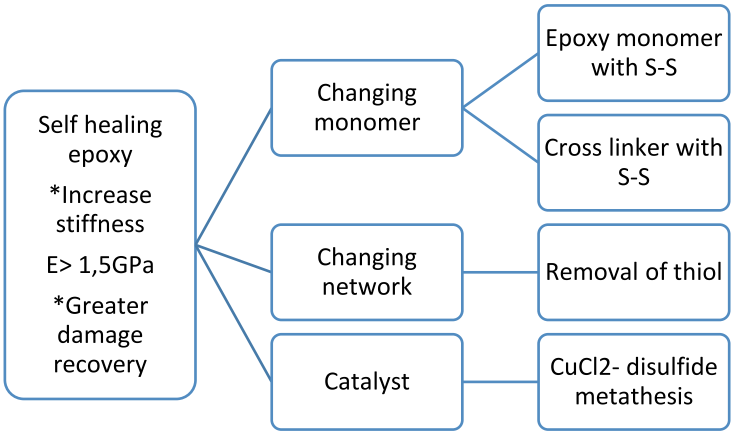


Figure 2-2 Schematic of the research plan to increase stiffness of the self-healing hybrid epoxy

2.1 Elimination of thiol

The organic network consists of DGEBA and Ancamine- 2500 network. However, it was observed that the tetra-thiol used to prevent phase separation and to promote thiol-disulfide exchange reactions also lead to side reactions with epoxies. Thiols in the presence of epoxies lead to a nucleophilic ring opening reaction with the epoxide groups similar to amines.

Epoxies consist of three-membered epoxide rings which are susceptible to nucleophilic attack. Thiols can participate in ring opening reactions by forming thiolate ions in the presence of a strong base. Stupara et al [24] and Fernández-Francos et al [25] both have studied this mechanism and found that in such a case, thiols are deprotonated though an acid-base proton exchange. These thiolate ions are strong nucleophiles which attack the epoxy ring and cause a ring opening, nucleophilic addition between thiolate and epoxy groups. This reaction is strongly autocatalytic due to the production of hydroxyl groups that further facilitate the ring opening reaction.[25] The mechanism is as shown in Figure 2-3. *This reduces the mechanical strength and stiffness of the epoxy due to lower strength of C-S (272 kJ/mol) when compared to C-N bond (305 kJ/mol).*

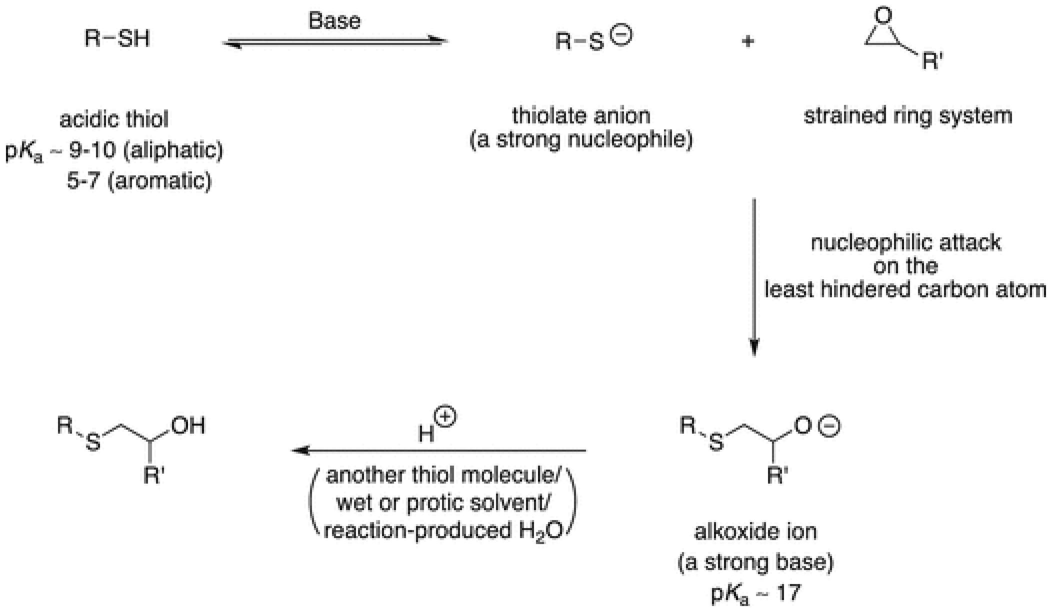


Figure 2-3 Thiol-epoxy reaction mechanism in the presence of a strong base [24]

Another problem with thiols is their thermal stability. Post et al observed the ability of the composite to heal multiple times reduced drastically when healed at 100°C when compared to healing at 85°C. Post et al postulated that the healing ability is not inexhaustible as temperatures above 70°C lead to slow oxidation of thiol groups which are known to assist the healing via reversible disulfide chemistry[22]. It is likely that above 70°C, thiolate ions which are required for a nucleophilic attack on disulfide bonds to lead to exchange reactions are oxidized to form disulfide bonds and hence there are no ions to aid healing.

This limits the curing and healing temperatures as temperatures above 100°C drastically reduce the thiolate ions available for healing. This low-temperature curing and healing also leads to lower mechanical properties. This is specifically a problem in structural epoxies which usually have a glass transition temperature above 80°C.

2.2 Addition of copper (II) chloride

Since thiols cannot be used as an efficient catalyst for disulfide healing at high temperatures over long periods of time, it was expected that removal of thiol leads to an increase in stiffness of the hybrid epoxy along with a possible reduction in healing efficiency. If there was a reduction in the healing efficiency, other catalysts for disulfide exchange reaction were explored.

Phosphines and rhodium have been studied in the literature as effective catalysts for disulfide metathesis, however, both have their own limitations. Phosphine is prone to oxidation and moreover is highly toxic. The high cost of rhodium prevents its large-scale use.

On the other hand, multiple metal halides have been shown to have complexation reactions with disulfides and hence have been used as a catalyst in oxidation or reduction of disulfides in literature. Boorman et al [26] studied the synthesis of different copper halides with organic disulfide and found that most of the halides were unstable except for copper(I) iodide-diethyl disulfide (Cul·Et2S2). Similarly, disulfides have been showed to form complexes with cobalt (II) and nickel (II) halides. Thus, the existence of a M-S bond has been clearly demonstrated, however in most of the cases, these complexes were studied for their stability and use as reduction or oxidation agents. The reversibility of the disulfide bond in the presence of these halides as catalysts is less widely studied.

Seff et al [27] studied the homolysis of the disulfide bond in dimethyl disulfide in the presence of cobalt (II) ions. They found that above 200°C, the disulfide bond underwent hemolysis and resulted in a S-bonded complex per unit cell. Heterolytic cleavage of the disulfide bond to yield RS- and RS+ ions was eliminated as there was no presence of any ions in the solution. This indicates homolytic cleavage of the S-S bond at 200°C in the presence of cobalt (II) ions to yield RS$^{\cdot}$ radicals.

More recently, Xiang et al used copper (II) chloride ($CuCl_2$) to catalyze disulfide exchange reactions in rubber in the presence of BTS and BDS. They found that disulfides underwent complexation with copper chloride to produce a new 4 membered S-S ring. However, at higher temperatures, the complex rearranges its bond length and arrangement and produces sulfenyl radicals.

2.3 Research questions

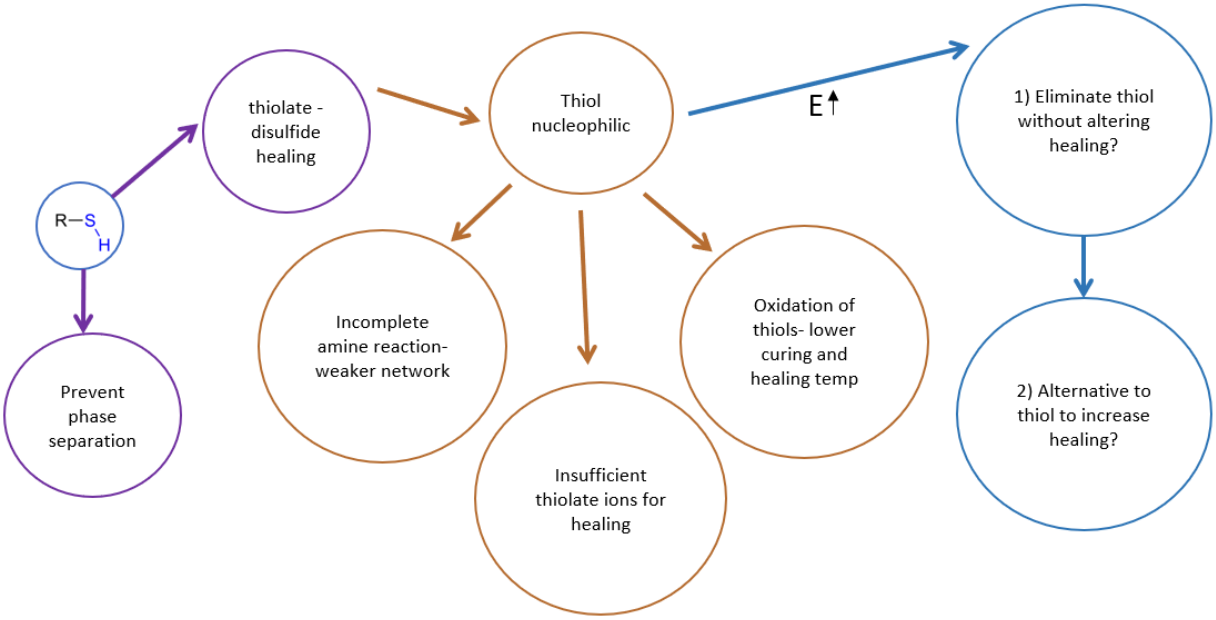


Figure 2-4 Schematic of problem statement showing the problems caused due to thiols when added to epoxy-amine systems and the research questions

Based on the problem statement, the following research questions have been formulated and were tested experimentally.

1) The hybrid epoxy composition studied by Wouter et al [28] uses thiols to prevent phase separation and promote metathesis. However, thiols cause a decrease in the mechanical properties of the epoxy and also limit the healing temperature to below 100°C.

- Can tetrathiol be eliminated from matrix preparation without phase separation?
- Can temperature triggered disulfide exchange reactions be studied for BDS in the absence of thiols?
- Can this exchange reactions be sufficient to allow macroscopic healing?

2) Based on the study of catalysts available, CuCl2 has the potential to be a cost-effective, high-temperature catalyst that promotes disulfide metathesis.

- Can dispersion and complexation of BDS with CuCl2 be ensured?
- Does CuCl2 catalyze the exchange reaction in the hybrid epoxy structure? If so what is the rate of exchange reaction compared to non-catalyzed and thiol catalyzed exchange reactions?
- Does CuCl2 also help in macroscopic healing?

Given the dearth of materials that do not compromise the mechanical properties to increase healing efficiency, being able to tune this hybrid epoxy by understanding the above hypotheses would help create an optimized self-healing epoxy that can change the attitude towards adoption of self-healing materials into commercial structural applications.

3 Effect of thiol on dual network relaxation and healing

In this chapter, the effect of the thiol content on the properties and healing behavior of dual networks is explored. Dual network disulfide-based epoxy systems with and without thiol were synthesized and characterized to understand the role of thiol in these systems. The following section explains the materials used along with the characterization techniques used.

3.1 Polymer preparation

To prepare the polymer networks, the same materials and polymer preparation methods used by Post et al were used [23].

Bisphenol A diglycidyl ether (DGEBA) in the form of Epon ™ 828 resin was purchased from Momentive. Ancamine®2500 curing agent was purchased from Air Products. (3- Aminopropyl) trimethoxysilane (97%), Pentaerythritol tetrakis (3-mercaptopropionate) and Triethylamine abbreviated as APTS, tetrathiol, and TEA from here on respectively were purchased from Sigma-Aldrich. Bis [3-(triethoxysilyl) propyl] disulfide (99%), from hereon called BDS was purchased from Capture Chemicals. All chemicals were used as received without further purification.

The weight ratios of the individual components are as shown in Table 1.

	Dual network epoxy without thiol (-thiol)	Dual network epoxy without thiol (-thiol)
Resin component	Weight ratio	Weight ratio
Epon 828	100	100
BDS	65	65
APTS	8	8
Ancamine 2500	58	58
tetrathiol	57	0
TEA	1	1

Table 1 Weight ratio of components in a) Dual network epoxy with thiol b) Dual network epoxy without thiol

Epon ™ 828, APTS and BDS were stirred for 3 hours at room temperature to allow the inorganic and organic parts to link. Ancamine® 2500 was then added and the mixture was manually stirred for 3 minutes. The resulting mixture and the tetrathiol were then degassed separately in a vacuum chamber for 10 minutes. Then, TEA and the degassed tetrathiol were added to the mixture and the final resin was manually stirred for another 5 minutes.

The mixture was then poured into a Teflon mold and was cured for 24 hours at room temperature. All the samples of required dimensions were cut and these samples were then cured for 60 hours at 100 °C under ambient pressure leading to films of about 1mm thickness as shown in Figure 3-1. The samples without tertrathiol showed some phase separation of BDS which was left as drops on the mold surface.

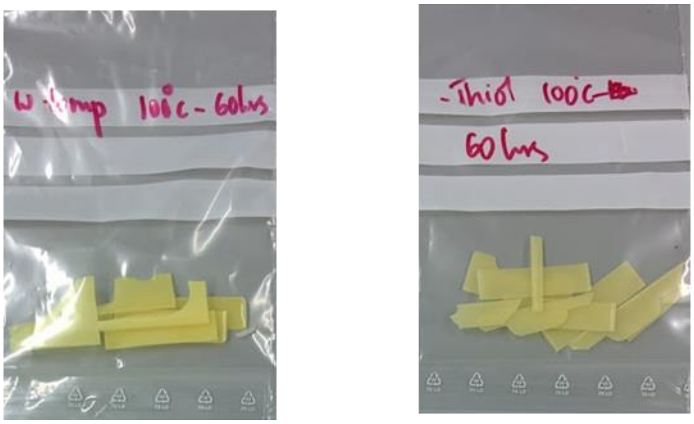


Figure 3-1 Free standing dual network polymer a) with thiol b) without thiol after curing for 60 hours at 100°C

3.2 Polymer Characterization

Mechanical Testing

The mechanical properties of the polymer network were studied according to ASTM D1708-13 using an Instron Model 3365 universal testing system equipped with a 1 kN load cell. Dog-bone micro-tensile specimens as shown in Figure 3-2 were loaded until failure at 2 mm/min at room temperature.

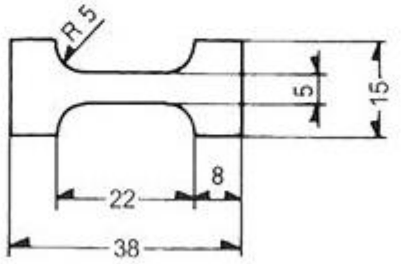


Figure 3-2 Sample size in (mm) of dog bone samples used for tensile testing as per ASTM D1708

Calorimetry

Differential Scanning Calorimetry (DSC) measurements were performed with PerkinElmer DSC 8000 under nitrogen. Sample weight of approximately 10 mg was used and heated from 25°C to 200°C at 10°C/min. For each sample, two heat- cool runs with the same heating/cooling rates were performed and the Tg values were determined using the inflection point of the DSC curves for the second cooling run.

Thermomechanical Testing

The thermomechanical properties of the polymer were measured using RSA-G2 Solids Analyzer Dynamic Mechanical Analysis (DMA) machine with samples the size of approximately 40*10*1 mm^3. The changes in Storage and loss modulus (E' and E") were measured by doing a temperature sweep from 25 to 200°C at a strain rate of 0.1%. Stress relaxation experiments were performed using the same DMA machine. A constant strain of 1% was applied and the corresponding stress was measured at room temperature (25°C), 80°C and 150°C.

Raman Spectroscopy

Raman spectroscopy tests were performed using a Renishaw inVia™ confocal Raman microscope with an exposure time of 15 seconds and 50 accumulations. Laser excitation line of 785 nm with 10% power was used. The spectral region from 445 to 3260 cm^{-1} was collected at three different temperatures (50,100,150 °C).. The temperature of the sample was controlled by a Linkam Scientific Instruments THMS600 hot-stage coupled to the Raman set-up, under atmospheric air. The hot stage was installed on the Raman stage. The samples were heated from room temperature to the desired temperature at a heating rate of 10 °C/min and kept at that temperature for 10 min for stabilization, prior to collection of the spectra.

The characteristic peak of S–S stretching at 510 cm^{-1} was measured along with the characteristic peak of C-C stretching at 1186 cm-^{1}. The C-C stretching peak was used as an internal standard and the amount of S–S bonds at each temperature by calculating the peak area ratio of the 510 cm^{-1} to the peak area of 1186 cm-^{1} similar to the method used by Abdolah Zadeh et al. [21]

DCB sample preparation and testing

GFRP laminates were produced using Epikote™ Resin 04908 and Epikure™ Curing Agent 04908 which were purchased from Hexion Specialty Chemicals. The selected glass fiber reinforcement was a woven HexForce® 7581 Fiber Glass Fabric, with a nominal areal weight of 303 g/m^{-2} and a fabric thickness of 0.23 mm purchased from Hexcel. GFRP laminates of 1mm were produced by infusing 8 layers glass fiber fabric with the selected epoxy resin as shown in Figure 3-3. The GFRP layers were cured for 16 hours at room temperature and post-cured for 8 hours at 80°C.

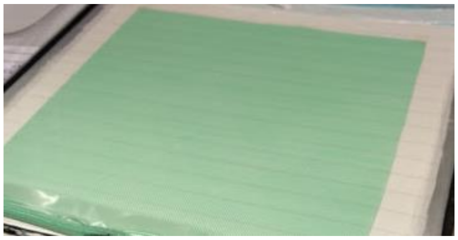


Figure 3-3 Fiber reinforced laminate fabrication

Dual network epoxy-GFRP laminates of 150x200 mm2 were produced by creating an interlayer made out of the epoxy dual networks with and without thiol in between 2 layers of GFRP as shown in Figure 3-4 a(left). A Teflon film of 60x200 mm2 was positioned midway between the dual network interlayer such that it created a pre-crack in the middle of the dual network interlayer. The stacking was then left in the oven to cure for 60 hours at 100°C. Finally, the resulting composite panel was cut into Double Cantilever beam (DCB) coupons of 150x25 mm2 prior to mechanical testing as shown in Figure 3-4 b(right).

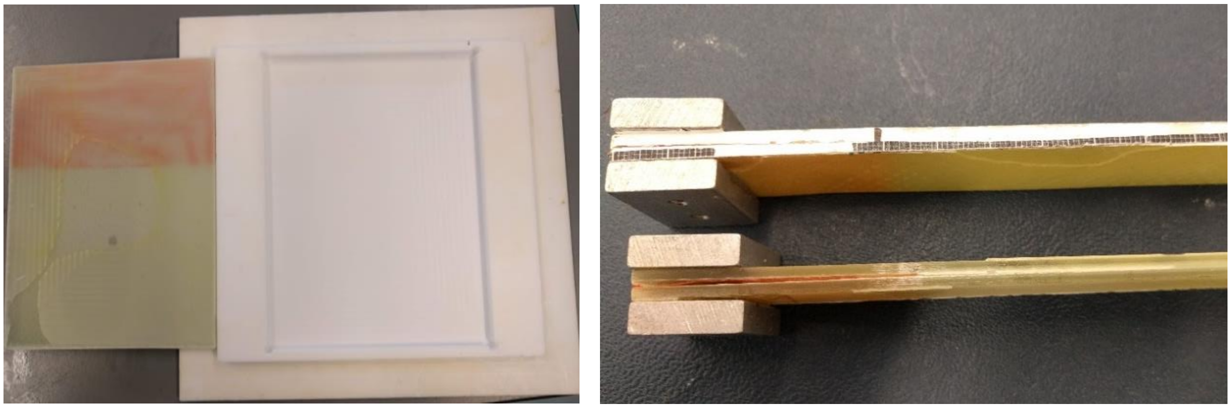


Figure 3-4 a) Mold using DCB laminates were prepared b) DCB coupons with the dual network epoxy interlayer showing a pre-crack at the center (red)

Mode I opening of DCB specimens was performed using Zwick mechanical testing machine (model 1455) equipped with a 20 kN load cell was used. The samples were tested at a constant crosshead speed of 5 mm/min and the test was stopped when a final displacement of 50 mm was achieved. The specimens tested by Mode I opening were healed at 5 bar pressure and 90°C temperature by placing them between silicon sheets to ensure uniform pressure over all the surfaces as shown in Figure 3-5.

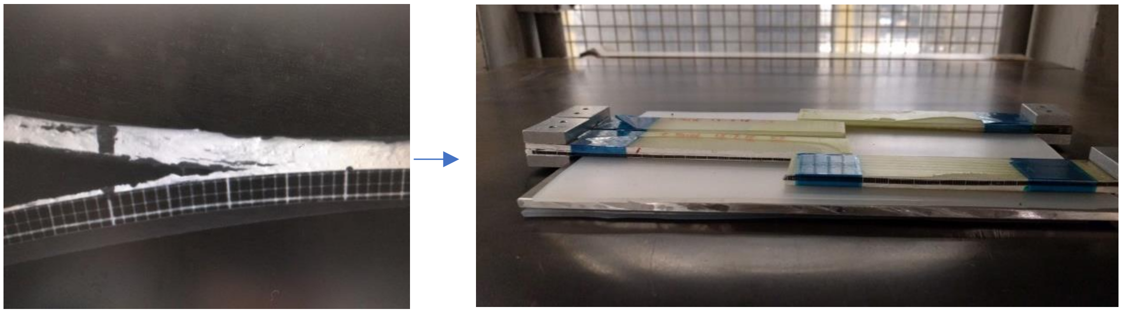


Figure 3-5 a) Crack propagation during DCB testing b) Crack healing in Joos press

3.3 Results and Discussion

3.3.1 Mechanical properties

Figure 3-6 shows the stress/strain curves of the dual networks with and without thiol. The stress-strain curves of both networks show a brittle failure, however, the dual network epoxy with thiol shows a greater plastic region when compared to the epoxy without thiol.

The Young modulus (E) of both polymers was calculated from their respective elastic regimes with the strain range from 0.002 to 0.010. The stress-strain curve of the polymer without thiol shows a higher Young's modulus of 1050MPa when compared to the polymer with thiol, which shows a modulus of 610 MPa. Similarly, the polymer without thiol has the higher tensile strength and lower tensile strain at break than the polymer with a thiol. This indicates that the absence of thiol leads to a more rigid network.

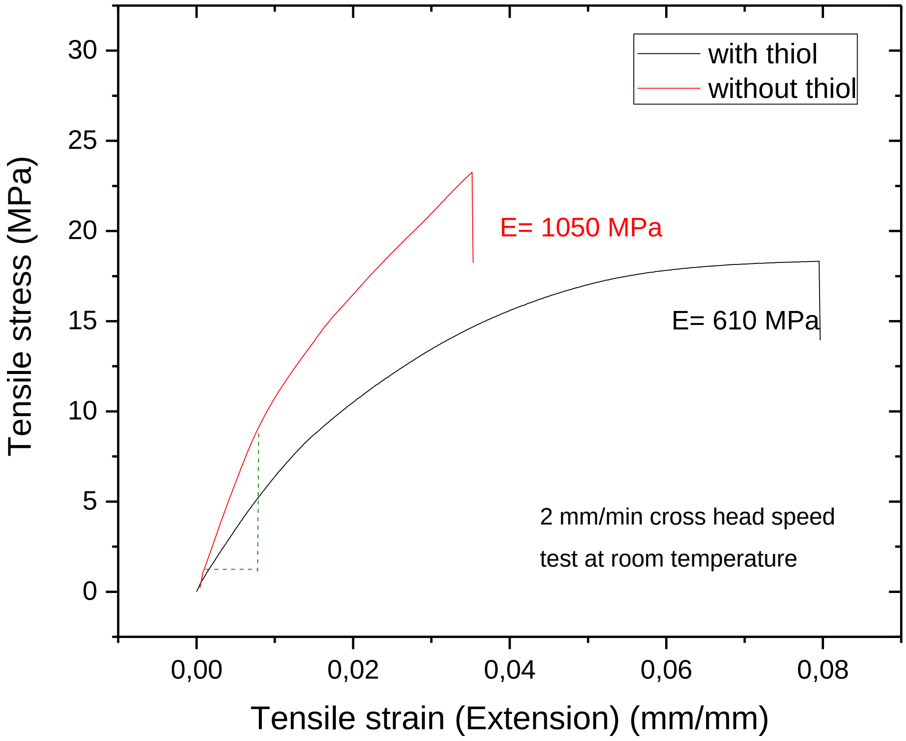


Figure 3-6 Stress Strain relation of polymer with and without thiol at room temperature

When tetrathiol is used in the dual network epoxy it can have 2 simultaneous reactions: 1) Tetrathiol can react with the S-S bonds in BDS to form new S-S crosslinks or 2) it can react with epoxy to cause ring opening reactions. Both cases lead to a reduction in the mechanical properties due to the lower bond strength of S-S and C-S compared to C-C. This can explain the increase in mechanical strength when the tetrathiol is eliminated from the dual network epoxy

3.3.2 Healing study

Given that the mechanical properties of the network improve on removing thiol, the next step was to study the polymer's healing behavior. In order to achieve macroscopic flow, there must be sufficient energy for the reversible bonds to break followed by sufficient energy for the broken polymer chains to move and promote healing. Thus, it is important to first understand the effect of thiol on the following two characteristic temperatures:

1. **Glass transition temperature T_g**: This is very similar to the other amorphous polymers. This is the temperature at which the polymer chains gain enough energy to undergo coordinated long-range molecular motion. At this temperature, there is a change from glassy to a rubbery state.
2. **Reversible reaction temperature T_r**: The reversible reaction temperature is the temperature at which the exchange reactions gain sufficient energy and mobility to create macroscopic relaxations and lead to a topology rearrangement and bond relaxation as shown in Figure 3-7. Thus, this temperature primarily depends on the Bond dissociation energy (BDE) of the disulfide bond, the energy barrier for the bond breaking and bond re-forming reactions and the availability of the disulfides bond.

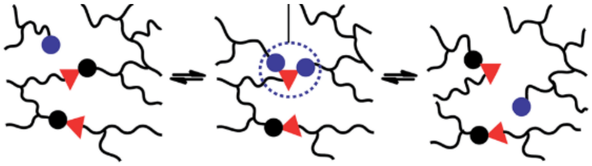


Figure 3-7 Schematic of reversible exchange reaction causing bond relaxation

For healing to occur, the healing temperature must be above both reversible reaction and glass transition temperature.

$T_{heal} > T_g$ and T_r → microscopic bond relaxation followed by macroscopic flow

3.3.3 Finding the glass transition temperature Tg

3.3.3.1 DSC results

Since the polymers networks were intended to be activated by heat, the thermal stability of the polymers was checked using Perkin Elmer TGA 4000. The polymers had negligible weight loss until 200°C indicating a thermal stability until 200°C.

The thermal transitions of the polymers were studied using Differential Scanning Calorimetry (DSC) from 25°C to 200°C. Normalized DSC plots after baseline correction for both polymers are shown in Figure 3-8.

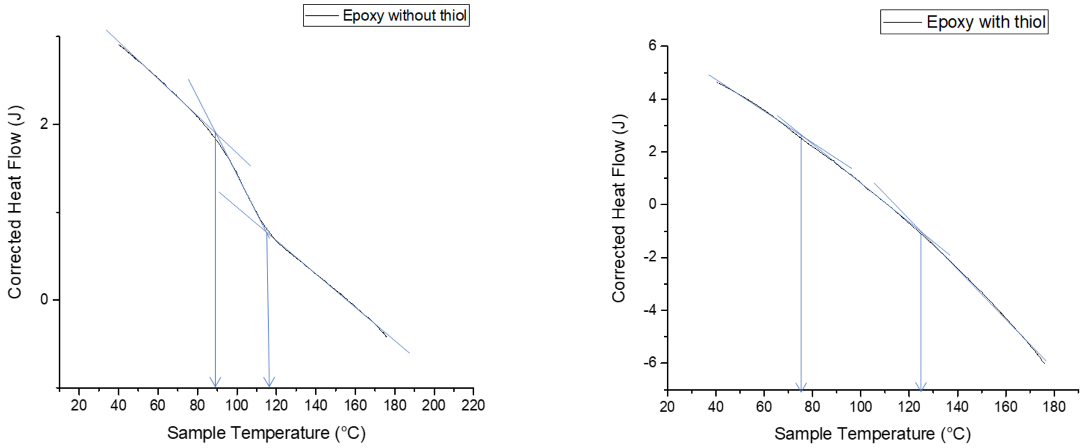


Figure 3-8: DSC curve of polymer with a) thiol b) without thiol

The dual network epoxy without thiol as shown in Figure 3-8 (left), shows a stepwise change in the heat flow response starting from 90°C and ending at 118°C. This indicates a glass transition temperature within that range and the Tg from half Cp extrapolated can be taken around 110°C.

The dual network epoxy with thiol as shown in Figure 3-8 (right) also shows a step wise transition between 78°C and 122°C. The transition begins at a lower temperature which coincides with mechanical testing results indicating a less rigid network. Once the transition beings, there is also a rapid decrease in the heat flow. The Tg from half Cp extrapolated can be taken around 100°C.

3.3.3.2 DMTA results

To get a better understanding of these transitions, DMA measurements were performed on both the dual network epoxies in single cantilever bending mode. A sinusoidal strain within the viscoelastic region of the dual network epoxy was applied and the corresponding stress was measured at different temperatures. This is used to determine the dynamic modulii such as storage (E’), loss modulus (E”) along with tan δ (E”/E’). The variations in these data give information about the various thermal transitions of the polymer.

Figure 3-9 a) shows the temperature sweep of the dual network epoxy without thiol carried on in single cantilever beam mode in the DMTA. The temperature sweep shows a tan δ peak beginning at 90°C and this corresponds with the data from calorimetry. This peak is broad and it extends to 120°C. The dual network epoxy with thiol shows a broad tan δ peak with two clear peaks at 80°C and 120°C as shown in Figure 3-9 b). These temperatures also coincide with the calorimetry data.

Both dual network epoxies show comparable storage modulus at room temperature, however, the drop in storage modulus in the hybrid epoxy with thiol occurs faster than that without thiol. In the dual network epoxy without thiol as shown in Figure 3-9 a), the E’ starts reducing at around 75°C, however, the drop in E’ in the hybrid epoxy with thiol is much earlier at around the temperature of 65°C as shown in C. This coincides with a weaker network probably due to greater S-S content leading to molecular chain motion at lower temperature.

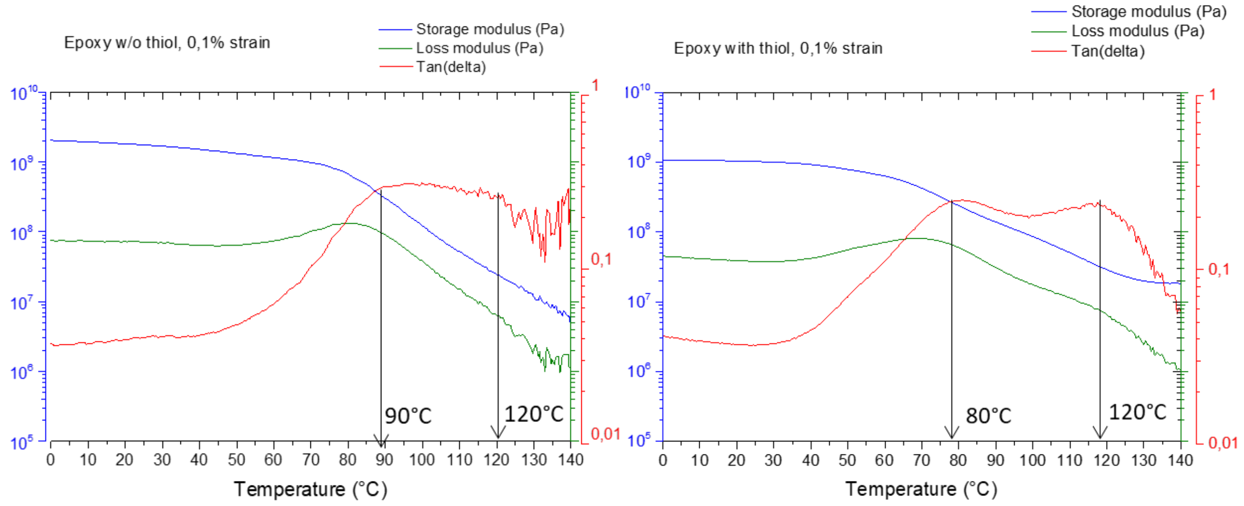


Figure 3-9: Temperature sweep in single cantilever beam mode of a) dual network epoxy without thiol b) dual network epoxy with thiol

To understand the origin of the broad tan δ peak, two hypotheses were thought of:

1) there could be an overlapping second transition corresponding to the temperature at which the disulfide bonds (S-S) undergo hemolysis to yield R-S$^{\cdot}$ radicals. This can be seen especially in the dual network epoxy with thiol Figure 3-9 b. which shows a clearer second peak probably due to the presence of greater number of S-S bonds, or
2) it could due to a mixture of different monomers in the commercial amine (Ancamine 2500) leading to the dual network having a broad glass transition temperature. To test these conditions, respective control samples were synthesized.

Control 1 [Octane control]: This epoxy consists of the same dual network structure as that of the epoxy without thiol, however, BDS is replaced with 1,8-Bis(triethoxysilyl)octane to eliminate all disulfide bonds. The structure of the 1,8-Bis(triethoxysilyl)octane is as shown in Figure 3-10.

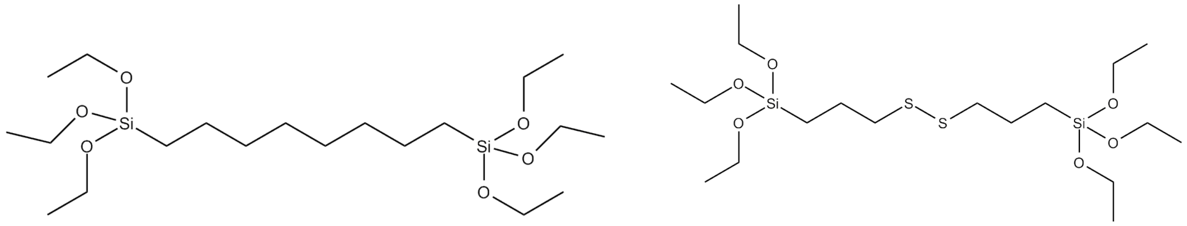


Figure 3-10 Chemical structure of a) 1,8-Bis(triethoxysilyl) octane b) Bis(3-triethoxysilylpropyl) disulfide (BDS)

Control 2 [Epon Ancamine control]: To test the possibility of the amine having multiple monomers leading to different glass transition temperatures, a control with just the epoxy and amine network was created.

The two control epoxies were tested in DMA single cantilever beam mode to find the tanδ peaks. The graphs are shown in Fig. The octane control displayed a similar double peak as shown in Figure 3-11 a. This indicated that the second tanδ peak was not due to the presence of disulfides. On the other hand, the Epon Ancamine control 2 displays a broad tan δ peak between 70 and 120°C as shown in Figure 3-11 b.

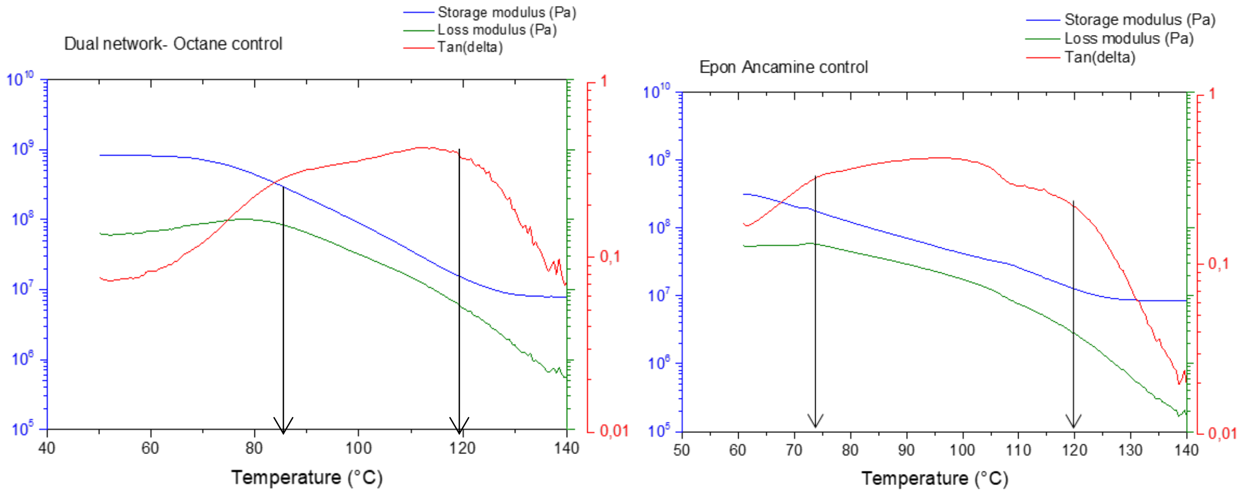


Figure 3-11 DMA temperature sweep of a) Octane control b) Epon Ancamine control

Thus it is likely that that the broad tan δ peak originates from the Ancamine 2500 due to a mixture of monomers, however, the dual network creation upon addition of the inorganic network (presence of Si-O-Si) network possibly leads to a second tan δ peak at 120°C. More research is required by peak de-convolution to understand the contribution of the amines vs inorganic network vs disulfides in the origin of various peaks, however, the main goal of this study was to understand the temperature required for healing.

From this, it was clear that both dual network epoxies had a wide range of glass transition temperatures due to the amine used. For both epoxies below 120°C there is some mobility in molecular chains, however, there is much more mobility above 120°C.

Healing at a temperature below 120°C allows only a part of the network to be mobile and hence the healing temperature should ideally be above 120°C to maximize polymer chain mobility and increase the healing efficiency. This temperature is particularly important in the case of epoxy without thiol as the higher rigidity of the network leads to lower chain mobility and macroscopic flow required for healing.

3.3.4 Finding reversible reaction temperature (Tr) and kinetics

3.3.4.1 Raman Spectroscopy

As mentioned before, sulfenyl radicals (R-S$^{\cdot}$) are crucial to healing and these radicals are created when disulfide bonds undergo homolysis in the presence of heat and/or catalysts. Raman spectroscopy was used to find the percentage of disulfides in the epoxy at different temperatures to gain a broad understanding of the temperature range in which the homolysis reaction occurred.

Figure 3-12 a) shows the Raman spectra of the dual network *epoxy without thiol* at different temperatures were normalized to the internal standard of C–C stretching peak at 1186 cm-^{1}. The characteristic peak of S–S stretching at 510 cm^{-1} was used to calculate the amount of S–S bonds at each temperature by calculating the peak area ratio of the 510 cm^{-1} to the peak area of 1186 cm-^{1} and is shown in Figure 3-12 b). [21]

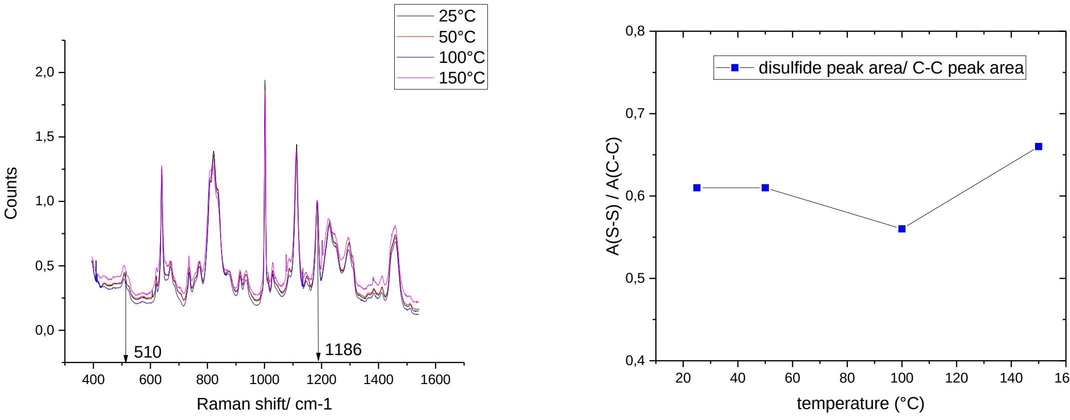


Figure 3-12 a) Raman spectroscopy of epoxy without thiol to study the effect of temperature on disulfide homolysis b) area of S-S peak to area od C-S peak at different temperatures

The area of S-S bond remains constant till 50°C. However, between 50 and 100°C, there is a drop in the area followed by an increase at 150°C. This could indicate disulfide homolysis at temperatures between 50 and 100°C causing a reduction in the area of S-S which coincides with the work done by Hernandez et al where they reported a hemolysis and sulfneyl radicals detection using ESR at 70°C [29].

The origin of the subsequent increase though is not very clear. Since there are no thiol involved into the reaction and there is no oxidation of thiols to give disulfides, this increase could be because Raman spectroscopy is a surface technique and at 150°C the epoxy become soft and rubbery, leading to a change in the S-S concentration at the surface or it could be an artifact caused due to changing the focus of the microscope due to the change in surface topology caused by glass transition.

3.3.4.2 Stress relaxation

Stress relaxation experiments involve applying a specific strain on the polymer rapidly and keeping it constant while measuring the stress as a function of time. Once the strain is applied, the length of the polymer is kept constant and thus there is no macroscopic movement of the body. Hence the relaxation in stress could be because of the following reasons: [30]

1. Chain Scission: When a polymer is strained above its elastic regime, the covalent bonds in the polymer can undergo scission. In this case of the dual network epoxy, it can lead to both permanent and reversible bonds breaking. This chain scission can thus cause a decrease in the stress experienced by the polymer by allowing for the broken chains to move and relax. The goal of this experiment is to measure the reversibility of the disulfide bonds without disturbing the permanent network and hence it has to be ensured that there is only shuffling in the reversible bonds without any damage to the permanent bonds. Thus, relaxation due to chain scission was avoided by doing the test within the elastic regime.

2. Relaxation due to glass transition: At the glass transition temperature (T_g), polymer chains gain sufficient mobility to undergo long-range coordinated motion. In thermoplastics, at the T_g, physical bonds and entanglements are broken allowing the polymer chains can slide past each other under stress continuously at sufficiently long time-scales. The time required for the polymer chain to move roughly its own size is known as the relaxation time. [5] Thus the largest polymer chain in the thermoplastics still has a finite relaxation time. Compared to this, thermosets are composed of one single crosslinked molecule and hence have infinite molecular weight and infinite relaxation time. In reality, thermosets undergo an initial partial stress relaxation due to the ability of the network to relax some stresses due to high temperatures. However, after this, they do not relax or have *non-finite relaxation time.*

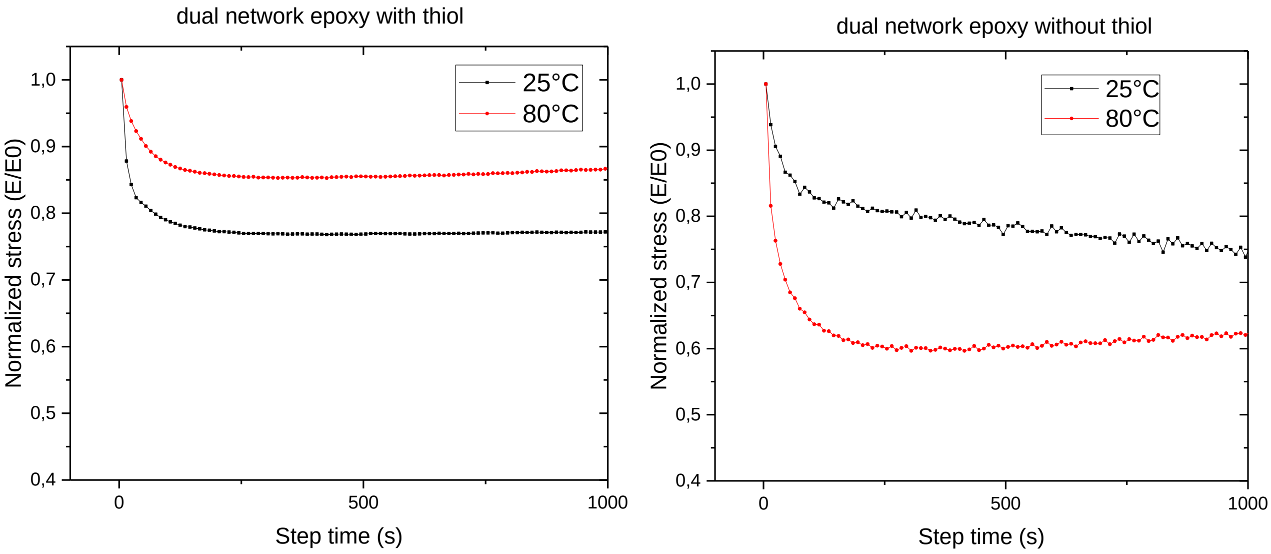
3. Relaxation due to bond interchange: Dynamic covalent networks have the ability to undergo reversible reactions to create covalent bonds that can constantly interchange. Hence reversible covalent networks must display properties between that of a thermoplastic and a thermoset in terms of relaxation times. They must be able to relax much more than that of a permanent network. This test thus can be used to test the reversibility of the exchange reactions and can be used to measure the kinetics at different temperatures. Stress relaxation experiments thus can be used to *study the microscopic shuffling of reversible bonds while keeping the polymer macroscopically intact.*

Stress relaxation experiments were thus used to identify the kinetics of disulfide bond shuffling. In order to prevent relaxation by chain scission, the strain to be applied was selected within the elastic regime of both epoxies. A strain of 1% or 0.01 was chosen to be applied after reaching the required temperature and stabilizing the sample for 10 minutes and the stress was monitored as a function of time.

Stress relaxation graphs for 25°C for the dual network epoxy with and without thiol are shown as black curves in Figure 3-13. Both the epoxies start with similar initial stress (~1.4MPa) as shown in the table below and relax to around 0.8 times the original stress. However, the graphs show the relaxation in the hybrid epoxy with thiol is faster than that without the thiol. The test was repeated and similar results were obtained.

Since thiols dissociate into thiolate ions at room temperature in the presence of Triethylamine (TEA), it is possible that there are much more ions then radicals at room temperature giving faster stress relaxation kinetics to the epoxy with thiol. However, it could also be the presence of a greater number of S-S in the hybrid epoxy with thiol which is easier to move (less rigid S-S bonds) compared to the network leading to more relaxation.

Stress relaxation at 80°C however, shows the opposite trend as the dual network epoxy with thiol shows lesser relaxation than that without. The dual network epoxy with thiol starts with a lower initial stress value(~0.15MPa) as shown in the table when compared to the hybrid epoxy without thiol (0.30MPa). Epoxy with thiol shows a 10% relaxation at 80°C compared to the 20% relaxation shown at room temperature as shown in by the red and black curves respectively in the Figure 3-13a. The epoxy without thiol, on the other hand, showed a 40% relaxation at 80°C as shown by the red curve in Figure 3-13b. *Thus, the dual network epoxy without thiol shows a higher stress relaxation at 80°C compared to that with thiol in spite of starting at a higher initial stress value.*



	Initial stress at 25°C (MPa)	Initial stress at 80°C (MPa)
with thiol	1.40	0.15
without thiol	1.38	0.30

Figure 3-13 Normalized Stress relaxation graphs of a) epoxy with thiol b) epoxy without thiol, at 25°C (black) and 80°C (red) , Table below showing absolute values of initial stress.

From these graphs, it was observed that the stress in curves at 80°C increases after some time. This can be observed by the upward trajectory of the red curves after 500s. This was expected to be the post-curing of the epoxies caused due to some unreacted groups which were not mobile enough to undergo a complete reaction. This was expected to be a possible cause for the anomaly in the relaxation behavior of the epoxy with thiol at 80°C being lower than that of 25°C.

To counter this problem, a post-curing step of heating the epoxy at 150°C for 1 hour well above the second transition temperature was used. This would make the entire network gain enough energy to be mobile and allow the inorganic reaction to complete. The epoxies were then examined using FTIR to observe the change in composition during the post-curing step. The 1100cm-1 peak corresponding to Si-OCH3 was measured to verify the change in the unreacted inorganic precursor. Using the C–H stretching band (2969 cm^{-1}) as the standard, the normalized peak intensity counts before and after the post curing are calculated and as shown in the table below. Both compositions show a drop in the 1100 cm^{-1} peak.

Si-OCH3 peak in FTIR at 1100 cm^{-1} :normalized intensity		
	60 hrs	post cure
Ep with thiol	3.8	3.5
Ep without thiol	2.65	2.37

Figure 3-14: FTIR analysis of the Si-OCH3 precursor before and after the post-curing

Once the effects of post-curing were eliminated, the disulfide bond exchange kinetics were re-examined at 80°C for the post-cured sample. The curves of stress relaxation of both epoxies are as shown in Figure 3-15.

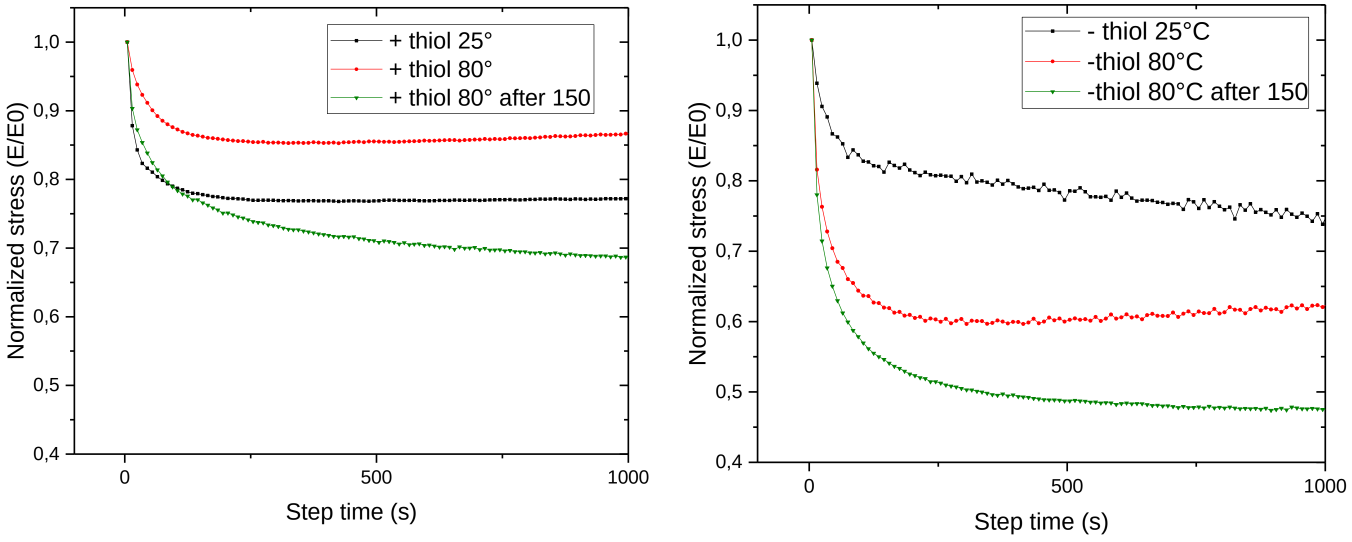


Figure 3-15 Stress relaxation graphs at 80 °C after post curing indicated by green lines for a) epoxy with thiol b) epoxy without thiol

The stress relaxation graphs now show distinct differences between the epoxies before and after post curing. Both hybrid epoxies show a greater percentage of stress relaxation at 80°C after post curing as shown by green curves when compared to the other two curves in Figure 3-15. The values of initial stresses of both hybrid epoxies remain almost the same as before post-curing with the epoxy without thiol showing the initial stress of 0.38MPa compared to the hybrid epoxy with thiol which shows 0.15MPa. The hybrid epoxy without thiol shows much higher stress relaxation of about 50% even though it starts with an initial stress of 0.38MPa.

In the hybrid epoxy with thiol, the rate of stress relaxation at 25°C is faster than that at 80°C. This coincides with literature which shows an oxidation of thiols at higher temperatures leading to slower relaxation. The relaxation kinetics of the hybrid epoxy without thiol, however, remain unchanged before and after post curing indicating no change in relaxation mechanism due to post-curing.

Usually, more elastic networks show greater relaxation due to the ease of the network to undergo thermal relaxation. However, the stress relaxation tests between the hybrid epoxy with and without thiol at 80°C after post curing (green curves in Figure 3-15) show that the dual network *epoxy without thiol which is more rigid shows higher relaxation than that of epoxy with thiol*. This behavior leads to the following possible inferences:

1) The dual network epoxy without thiol undergoes significant stress relaxation (50%) at 80°C. For stress relaxation to happen, since other factors such as chain scission and the effect of Tg have been eliminated, the origin of relaxation must be from *reversible bond exchange reactions* causing network relaxation.
2) In this dual-network epoxy without thiol, the most possible mechanism of these exchange reactions is *thermally mediated radical exchange reaction* as shown in Figure 3-16. This is proposed as there is no presence of thiolate ions created from thiols in the dual network epoxy without thiol and yet the network is able to relax. On the other hand, the creation of sulfenyl radicals has been studied in Raman studies which have been supported by multiple papers in the literature. [29],[16], [18].
3) There is sufficient radical generation at 80°C to these radical mediated exchange reactions. The greater shuffling kinetics without thiol show that there is at least the same number of radicals created in the dual network epoxy without thiol as that of the dual network epoxy with thiol helping in shuffling.

$$\mathrm{RSH} \rightleftharpoons \mathrm{RS}^- + \mathrm{H}^+ \quad (\mathrm{p}K_\mathrm{a}^{\mathrm{RSH}})$$

$$\mathrm{RS}^- + \mathrm{R'SSR'} \rightleftharpoons \mathrm{RSSR'} + {}^-\mathrm{SR'}$$

$$\mathrm{H}^+ + {}^-\mathrm{SR'} \rightleftharpoons \mathrm{HSR'} \quad (\mathrm{p}K_\mathrm{a}^{\mathrm{R'SH}})$$

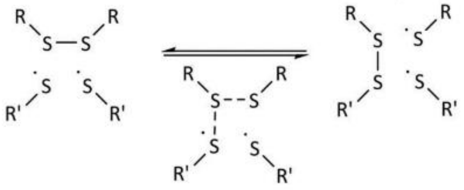


Figure 3-16 Thiol-disulfide exchange reactions vs radical mediated disulfide exchange reaction- most likely mechanism of stress relaxation in the dual network epoxies is radical-mediated mechanism.

In conclusion, these experiments show that the radical generation and disulfide bond shuffling in the absence of thiol at 80°C is not lower than that in the presence of thiol; in fact, there is greater relaxation in the absence of thiol. Some possible explanations of this behavior are mentioned in Appendix B. Thus, if the other factors are kept constant, epoxies without thiol should be able to heal as well as or better than that of epoxies with thiol.

3.4 Healing macroscopic damage

One of the biggest challenges is to quantify the macroscopic healing efficiency keeping in mind that these polymers require high temperatures and pressure to create enough macroscopic mobility to heal large-scale damages. Various methods were tried to test the healing efficiency. The epoxies were made into films of 1mm thickness in Teflon molds and broken. The broken ends were put together as shown in Figure 3-17a) and pressure was applied from the top using the top half of the mold and the epoxies were left in the oven to heal. However, at the end of the healing cycle, it was observed that sufficient contact was not maintained in between the two parts due to the shrinking of the epoxy when they cure and heal making them smaller than the mold in which they were cast in.

Another method that was used by Post et al was to create a GFRP reinforced with the reversible epoxy as shown in Figure 3-17b. This GFRP was then cut into specimens for 3-point bending, double cantilever beam (DCB) and impact testing. However, each plate of GFRP required around 600g of the reversible epoxy. This required a lot of material and hence was not very feasible to use to test multiple epoxy chemistries.

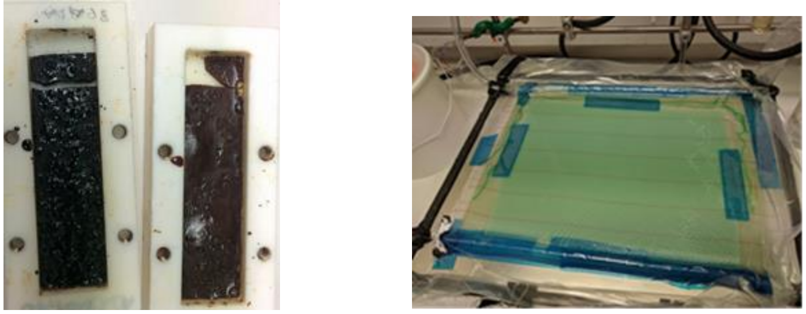


Figure 3-17 a) Broken pieces of epoxy in a Teflon mold with pressure applied from the top: insufficient contact maintained due to shrinkage of epoxy at high temperatures b) GFRP infused with the reversible epoxy under vacuum

In order to overcome this problem, a mold was created to create an interlayer of the reversible epoxy along with a pre-crack as shown in Figure 3-4 and tested in Mode I opening using a double cantilever specimen as shown in Figure 3-18.

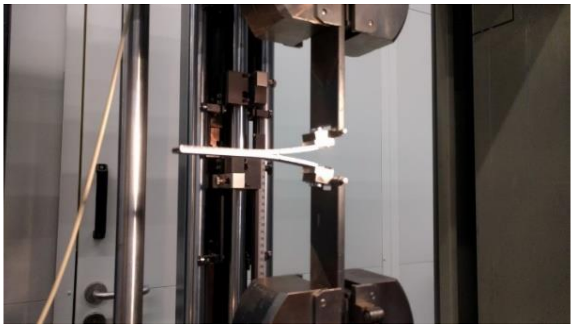


Figure 3-18 DCB (Mode I)Testing

Figure 3-19 a) shows the load-displacement curves of the mode I opening of GFRP samples with the pristine epoxy interlayers. The pristine hybrid epoxy without thiol shows higher maximum load (70N) when compared to the hybrid epoxy with thiol (40N) as shown in Figure 3-19 a) and is in coherence with the mechanical testing results shown in Figure 3-19 b).

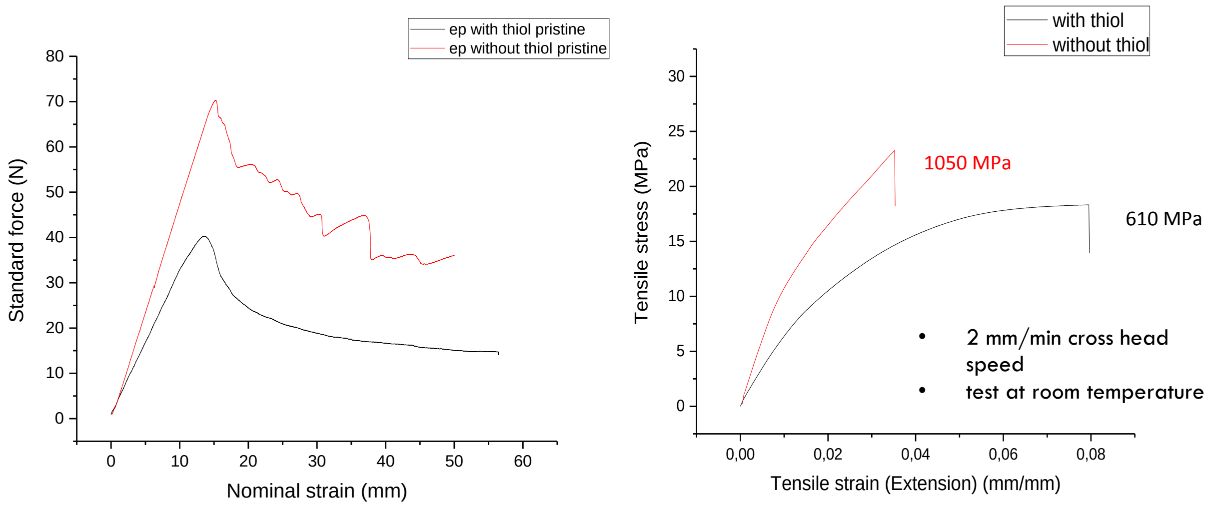


Figure 3-19 a) Load-displacement curves of mode I DCB opening b) Tensile testing of epoxy with thiol (black) and epoxy without thiol (red

Macroscopic healing in dual network epoxy without thiol

After the crack was opened completely to separate the two halves, the specimen was healed at **90°C for 16 hours at 5 bar pressure**. The healed sample is shown in Figure 3-20.

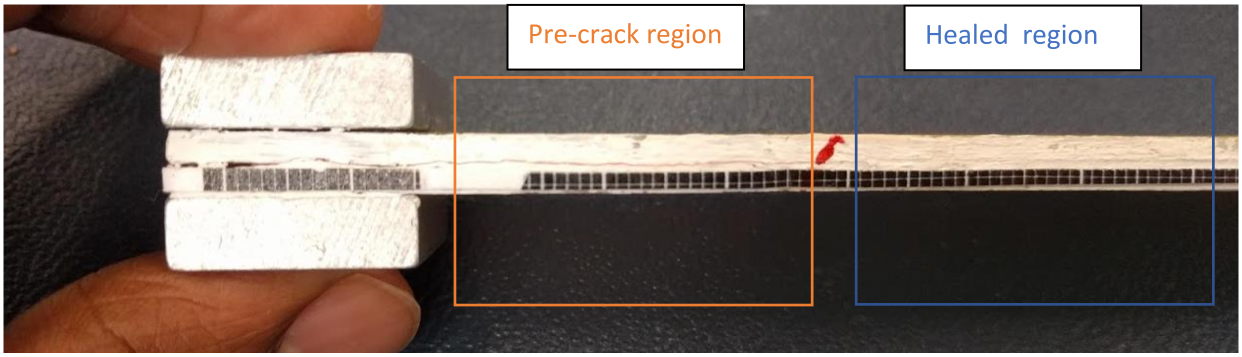


Figure 3-20 DCB sample of dual network epoxy with thiol healed at 90°C showing crack disappearance after the pre-crack region marked by red.

The healing behavior of the dual network epoxy with thiol is as shown in Figure 3-21. The black curve shows the load-displacement behavior of the pristine epoxy. The red curve shows the mode I opening of the sample after the 1st cycle of healing. It can be observed that there is a very high recovery in the maximum load (about 33N) at the beginning followed by crack opening at the same rate as in the pristine sample.

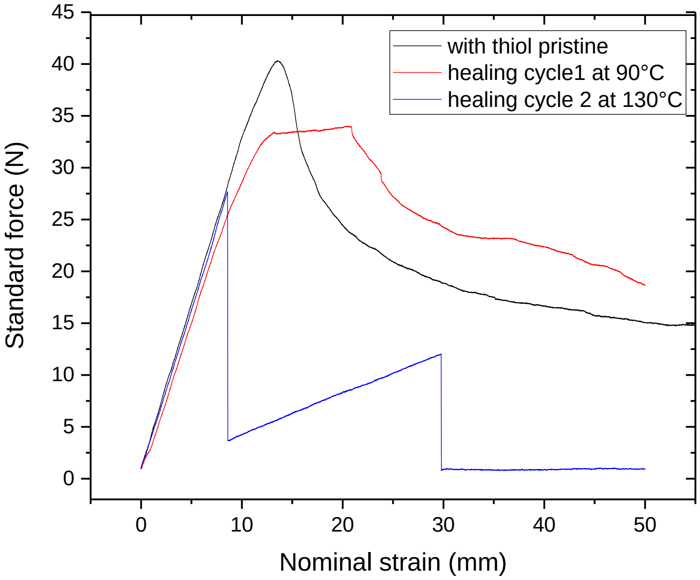


Figure 3-21 Load displacement curve of dual network epoxy with thiol

The load-displacement curve of this dual-network epoxy healed for the second time, but this time **at 130°C for 16 hours at 5 bar pressure** is shown as a blue curve in Figure3-21. When the same sample was healed for a second cycle at 130°C to increase the mobility of the network by going above its Tg, it was observed that the sample regained the initial resistance to crack opening as seen by the rise in maximum force (~27N) at the same slope as a pristine sample. Once the crack opens, however, the crack propagates very quickly with much lesser resistance to the crack growth till a displacement of 30mm after which it opens completely showing no resistance to crack growth.

To distinguish the effect of post-curing from healing, the same test was repeated with a new sample but after initial testing, the sample was post-cured for 1 hour at 130°C to ensure the completion of any unreacted groups. Then, the same healing and testing conditions as before were used. The healing behavior of this post cured dual network epoxy with thiol is as shown in Figure 3-22.

It can be observed that after post curing, healing at 90°C for 16 hours leads to an initial recovery in resistance to crack propagation and recovery in maximum force similar to the previous sample without post-curing. However, the max. force regained is about 27 N as shown in the red curve of Figure 3-22 compared to a max force recovery of 33N in the non-post-cured sample shown in Figure3-21. The crack propagation of post-cured sample healed at 90°C (red curve) goes much quickly than when compared to the non-post cured sample. This indicates that before post-curing, the epoxy had some unreacted groups which react and lead to complete healing and cause new crack growth, however once post cured, the crack growth is much faster due to the crack not being able to recover its properties completely.

After the second healing cycle at 130°C, the dual network shows a similar recovery in resistance to crack growth and max force in the beginning. This shows the ability of the epoxy to heal multiple times.

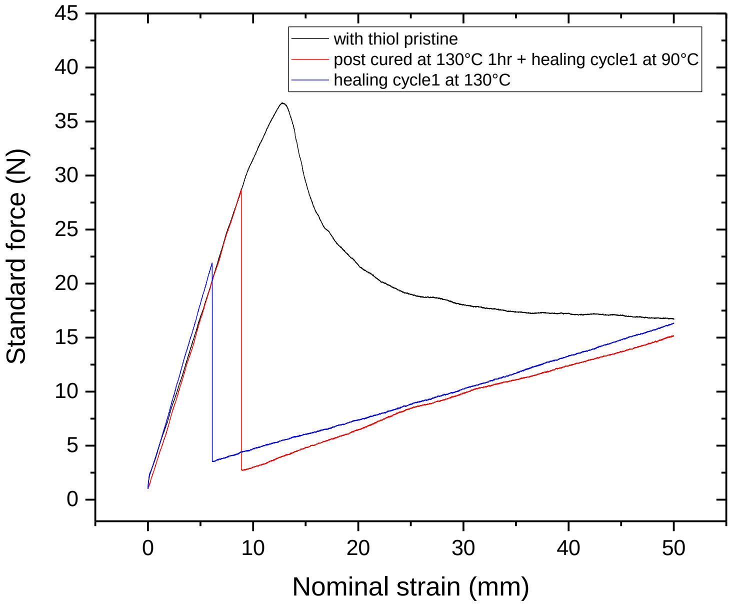


Figure 3-22 Load-displacement curves of dual network epoxy with thiol post-cured at 130°C

Macroscopic healing in dual network epoxy without thiol

To study the effect of removing thiol on the macroscopic healing behavior, similar DCB samples with the dual network epoxy without thiol were made. The black curve in Figure 3-23 indicates the pristine curve and it shows a maximum force of 70N.

The macroscopic healing behavior of the dual network epoxy without thiol, however, is very different from its stress relaxation behavior. When healed at 90°C for 16 hours at 5 bar pressure the hybrid epoxy without shows no initial recovery of resistance to crack growth and the crack opens immediately as shown by the red curve in Figure 3-23. However, as the crack reaches closer to the tip, it shows an increase in resistance to crack growth. At around 45mm displacement (nominal strain), it shows a maximum force of around 35N and then the crack reopens suddenly and further, it shows very low resistance to crack propagation after that.

The sample was then healed to 130°C for 16 hours at 5 bar pressure. The load-displacement curve is as shown in the blue curves. Healing at 130°C shows not much difference in terms of initial recovery of the maximum force as the crack opens similarly very quickly in the beginning and slows down as it approaches the crack tip.

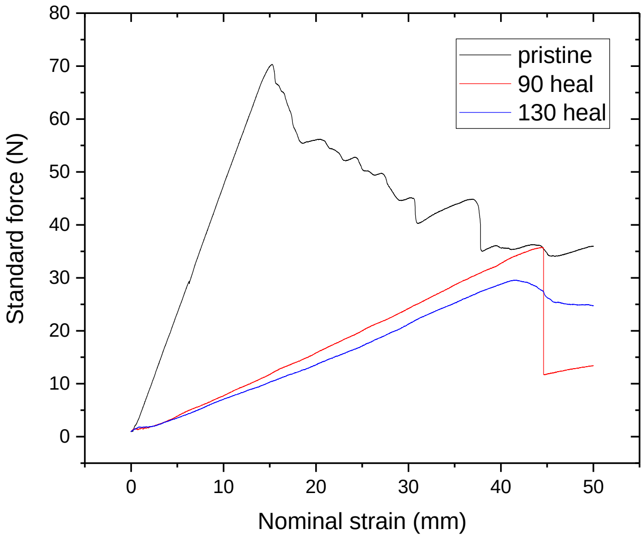


Figure 3-23 Load-displacement curves of dual network epoxy without thiol tested in mode I opening

The macroscopic healing of the epoxy without thiol is thus much lower than that of the epoxy with thiol. One of the main reasons why the healing efficiency is lower when compared to the epoxy with thiol is the number of disulfide bridges present. The epoxy with thiol has much greater S-S bond content as the thiols help in preventing phase separation of the BDS by reacting with it to create much more S-S bonds. When tetrathiol is removed, one there are no new bonds of S-S created as there is no reaction with thiols 2) the amount of BDS in the epoxy is also lesser as a part of the BDS phase separates from the mixture during casting the films.

This lower S-S content leads to two things:

1) insufficient microscopic flow at a higher temperature, as there aren't enough reversible bonds present to allow for macroscopic healing
2) The higher rigidity of the network due to lower S-S bonds. C-C bonds being stronger than C-C makes the network more rigid reducing even further the macroscopic healing due to reduced flow of the network. This can explain why there is a higher max force recovery close to the crack opening tip, as the polymer chains require lesser mobility to align perfectly near the tip than at the edge.

In conclusion, it can be said that macroscopic healing of large-scale damages (>cm^2) requires sufficient reversible bond content along with network flexibility to allow for macroscopic flow. The reversible bond should be able to have been sufficiently activated at the healing temperature and must be distributed throughout the architecture of the network to create enough flow.

3.5 Summary

- The role of tetra-thiol in a dual network disulfide-based epoxy developed for aerospace applications has been studied.

- Mechanical properties of the dual network epoxy decrease in the presence of thiol indicating the development of a less rigid network.

- Stress relaxation experiments at 80°C shows that the dual network epoxy without thiol has greater relaxation than the dual network epoxy with thiol, in spite of having a more rigid network.

- Raman analysis and stress relaxation experiments are in agreement with the literature and suggest that the most likely mechanism for exchange reactions in this dual network epoxy is thermally activated radical-mediated mechanism after sulfenyl radical creation by homolysis.

- Eliminating thiol, however, also reduces the macroscopic healing of large scale damages due to a decrease in the net S-S content and lower macroscopic mobility.

4 Effect of $CuCl_2$ on thiol-free dual network relaxation and healing

Since the dual-network epoxy without thiol showed much lesser macroscopic healing, alternatives were explored to see if the reversibility of the network can be regained by using a different catalyst. To do so a catalyst that prevents the phase separation of disulfides was explored. As mentioned before, metal halides have been shown to form M-S bonds via complexation. However the use of metal halides as catalyst for disulfide exchange reactions is relatively unexplored.

Xiang et al [31] in 2015 reported for the first time the use of $CuCl_2$ as a cost effective, heat resisting, oxygen insensitive catalyst to trigger di- sulfide metathesis in vulcanized rubber. The mechanism of disulfide metathesis was studied to be a $CuCl_2$-based complex catalysis instead of radical or ion intermediates. When $CuCl_2$ and disulfides are mixed, the lone pair electrons of sulfur atoms in disulfides interact with the vacant 3d orbital of Cu(II) and form an intermediate complex as shown in Fig 36. This system enters a transient state by optimizing the spatial conformation of the complex- adjusting the bond angle and bond length between disulfide and $CuCl_2$. This complex then fractures at 110°C due to the localization of electrons of disulfide bonds. These fractured sulfur atoms form a new disulfide bond keeping the $CuCl_2$- disulfide complex intact. The schematic of this process is shown in Figure 4-1. This newly generated complex interacts with another disulfide bond and the process repeats. [31] Thus the healing mechanism is expected to change to a 2+2 associative metathesis as shown in Figure 4-2.

Stress relaxation experiments were performed by Xiang et al on vulcanized rubber with BDS and it was observed that the rubber with BDS and $CuCl_2$ relaxed above 110°C. However, this catalyst has not been tried in other compositions and hence remains to be verified.

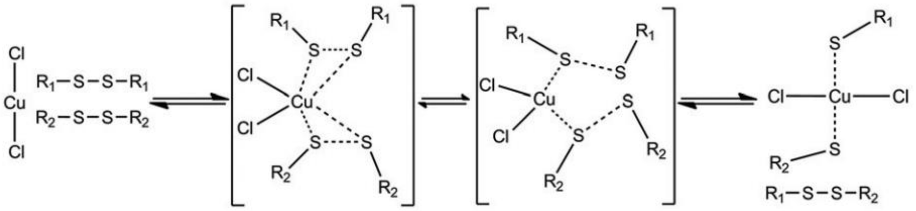


Figure 4-1 Disulfide metathesis through CuCl2 complexation [31]

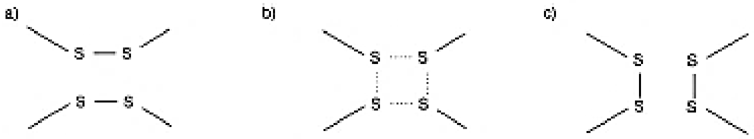


Figure 4-2 2+2 associative metathesis

4.1 Complex formation

One of the key factors to compare this healing mechanism was to study the formation of copper complex with disulfides. Given that this system has other component such as APS and Ancamine which can form a complex with copper chloride, it was important to verify if the disulfides form a complex.

Since transition metals like copper display specific colors when they form a complex with different elements, the color of the resulting mixture was observed to study complex formation with disulfides. Copper chloride was mixed with each of the individual components to see the interaction. It was observed that copper chloride formed instantaneously a distinct deep blue complex with APS. This is due to the formation of a copper-ammonia complex as shown below. This complex is known to have this deep blue color that is being displayed on the left side of Figure 4-3.

$$[Cu(H_2O)_6]^{2+}(aq) + 4\ NH_3\ (aq) <==> [Cu(NH_3)_4(H_2O)_2]^{2+}$$

When copper chloride was mixed with BDS, it showed much higher agglomeration and separation. The liquid however is faintly colored by dark green color as shown in Figure 4-3. This color is most likely from the complex formation from the disulfides and copper chloride. Keeping these two references in mind, the individual components were mixed and the color was observed. In the beginning, the mixture of Epoxy +APS + BDS+ CuCl2 shows the same bright blue color as the one displayed by CuCl2 and APS. This indicates that the reaction between copper chloride and APS is very quick. However, after 24 hours at room temperature, the mixture turns to a dark green color similar to that of the BDS+ CuCl2 complex as shown in Figure 4-3. This indicates that the complex formation of CUCl2 with APS is much quicker than the complex formation with BDS, however in time, there is sufficient interaction with the S-S bonds.

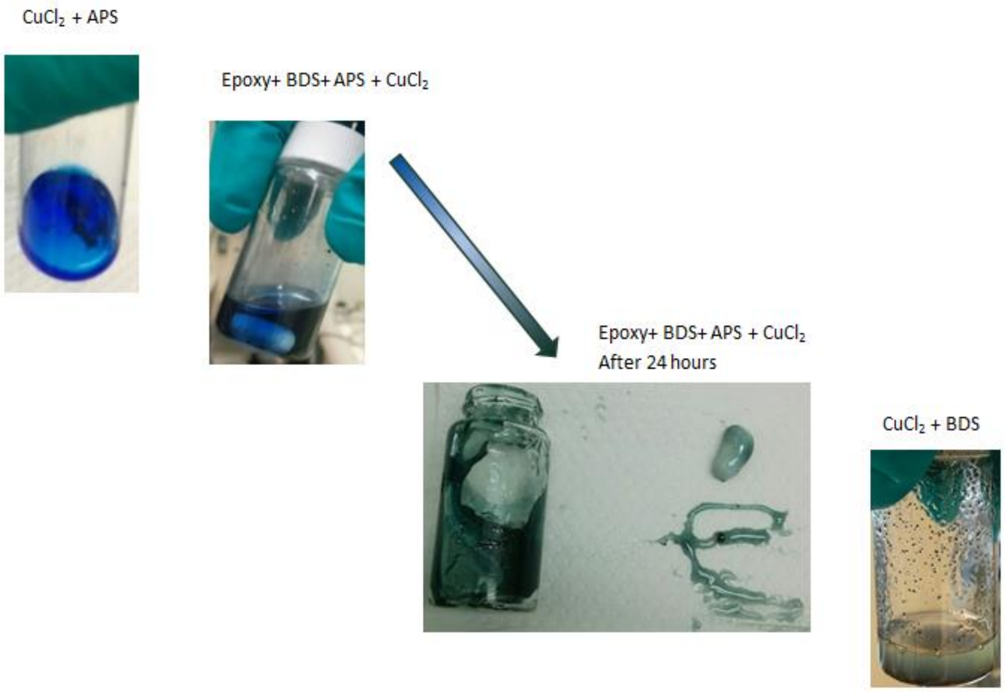


Figure 4-3 Complex formation of CuCl2 with APS and BDS along with the development of complex in the mixture

4.2 Polymer preparation and characterization

The polymer preparation method is the same as that mentioned in sectioned 3.2 except for the addition of CuCl2 to the epoxy-BDS-APS mixture before the addition of the amine. Epon ™ 828, APTS and BDS and CuCl2 were stirred for 3 hours at room temperature to allow the inorganic and organic parts to link. Ancamine® 2500 was then added and the mixture was manually stirred for 3 minutes. The resulting mixture and the tetrathiol were then degassed separately in a vacuum chamber for 10 minutes. Then, TEA and the degassed tetrathiol were added to the mixture and the final resin was manually stirred for another 5 minutes. The weight ratio of all resin components is depicted in Table2

The mixture was then poured into a Teflon mold and was cured for 24 hours at room temperature. All the samples of required dimensions were cut and these samples were then cured for 60 hours at 100 °C under ambient pressure leading to films of about 1mm thickness as shown. The cured samples are as shown in Figure 4-4.

The same characterization techniques as described in section 3.2 were used to study this epoxy.

	Dual network epoxy without thiol (-thiol)	Dual network epoxy without thiol with $CuCl_2$ (+ $CuCl_2$)
Resin component	Weight ratio	Weight ratio
Epon 828	100	100
BDS	65	65
APTS	8	8
Ancamine 2500	58	58
tetrathiol	0	0
TEA	1	1
$CuCl_2$	0	1

Table 2 Weight ratio of components in a) Dual network epoxy without thiol b) Dual network epoxy without thiol+ CuCl2

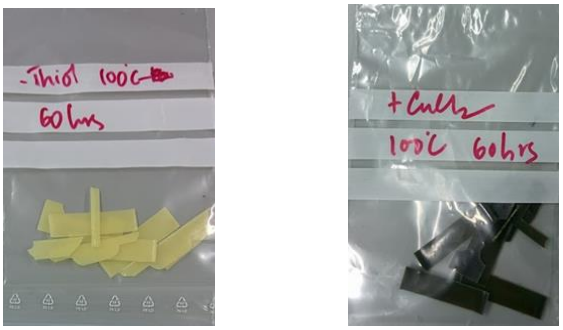


Figure 4-4 Free standing polymer samples showing difference in color after addition of CuCl2

4.3 Results and Discussion

4.3.1 Mechanical properties

The stress strain graphs in Figure 4-5 show the mechanical behavior of the hybrid epoxy without thiol in the presence and absence of copper chloride. Both the dual-network epoxies show very similar behavior in terms of both networks showing an initial elastic region followed by a short plastic region and subsequent brittle failure.

The modulus of both polymers where calculated in their respective elastic regimes with the strain range from 0.001 to 0.01. Both polymers show very similar Young's modulus with the hybrid epoxy with $CuCl_2$ showing a slightly higher E modulus of 1130MPa when compared to the epoxy without $CuCl_2$ which shows a modulus of 1050 MPa. The proposed mode of disulphide exchange is a 2+2 mechanism as mentioned before. This means that the S-S bonds are attached to each other to form 4 membered rings along with CuCL2. This could be the reason for the small increase in Young's modulus E.

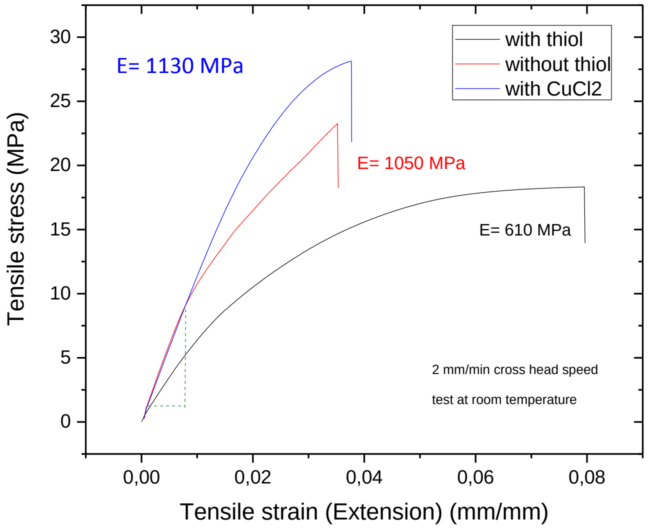


Figure 4-5 Stress Strain relation of polymer without CuCl2 (red) and with CuCl2 (blue) at room temperature

4.3.2 Relaxation and healing in presence of $CuCl_2$

4.3.2.1 DSC results

TGA analysis of the polymers indicates that both polymers have negligible weight loss till 200°C. The thermal transitions of the polymers were studied using Differential Scanning Calorimetry (DSC) from 25°C till 200°C. Normalized DSC plots after baseline correction for both polymers are shown in Figure 4-6.

Both the polymers show very similar behavior with a step wise change in the thermal behavior beginning at around 85°C and ending at 120-125°C . Since the same epoxy-amine system is used, it is likely that copper chloride doesn't interfere with the epoxy-amine reaction and hence the thermal transitions begins at the same temperature. The small increase in the end of transition can be attributed to the increase in S-S bonding increasing the inorganic network transition temperature.

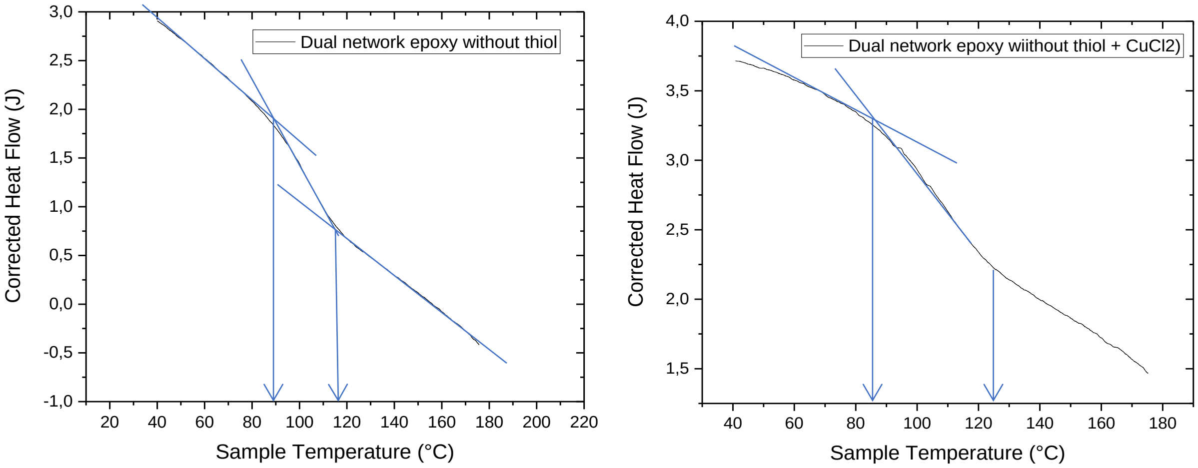


Figure 4-6 DSC plot of dual network epoxy without thiol 1) without CuCl2 b) with CuCl2

4.3.2.2 DMA results

The thermo-mechanical properties of both the polymers were studied using DMA in single cantilever beam mode. Figure 3-9 a) shows the temperature sweep of the dual network epoxy without thiol carried on in single cantilever beam mode in the DMTA. The temperature sweep shows a tan δ peak beginning at 90°C and this corresponds with the data from calorimetry. This peak is broad and it extends to 120°C.

The dual network epoxy with CuCl2 shows a broad tan δ peak with two peaks at 90°C and 120°C as shown in Figure 3-9 b). This behavior is similar to that of the DMA transitions while using thiol. This could be because both thiol and bind with disulfides to create new crosslinks.

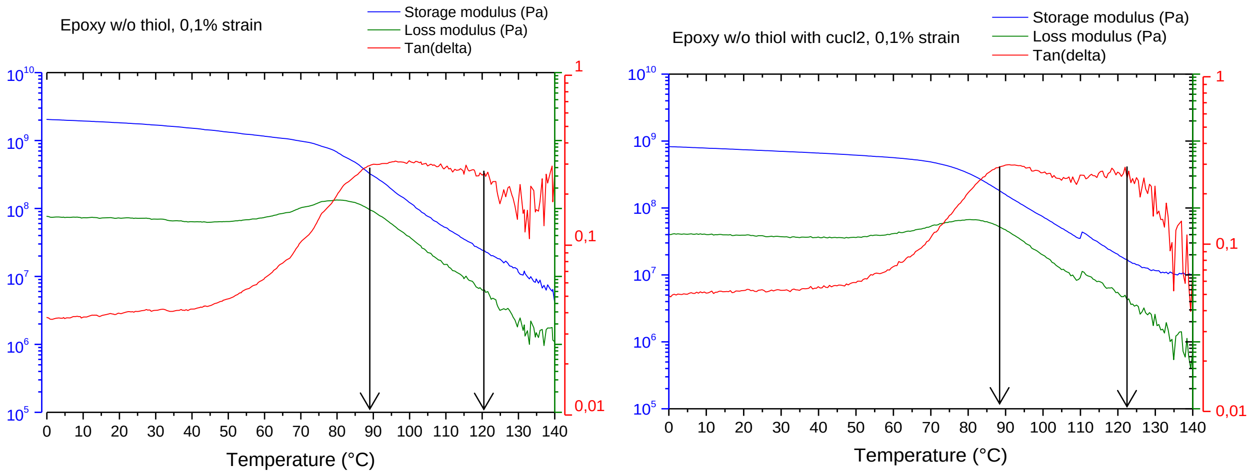


Figure 4-7 DMA plot in single cantilever beam mode of epoxy without thiol 1) without CuCl2 b) with CuCl2

4.3.2.3 Stress relaxation experiments

Stress relaxation experiments were performed to study the S-S bond reversibility kinetics in the presence of copper chloride. It is observed that the relaxation of polymer with copper chloride is lesser at room temperature compared to the polymer without the copper chloride (black curves in Figure 4-8). $CuCl_2$ increases stiffness possibly due to an interaction between SS and $CuCl_2$ and hence it is likely that the relaxation kinetics reduce at room temperature in the presence of copper chloride.

However, the relaxation at higher temperature 80°C is similar to that of the dual network epoxy without thiol and is shown by the red curves in Figure 4-8. It relaxes to about 60 % of the initial stress with almost similar relaxation times.

Both the polymers were then post-cured at 150°C for 1 hour similar to the previous experiments. After post-curing, the stress in the dual network epoxy with CuCl2 relaxes to 40% of its initial value as shown by the green curve in Figure 4-8.

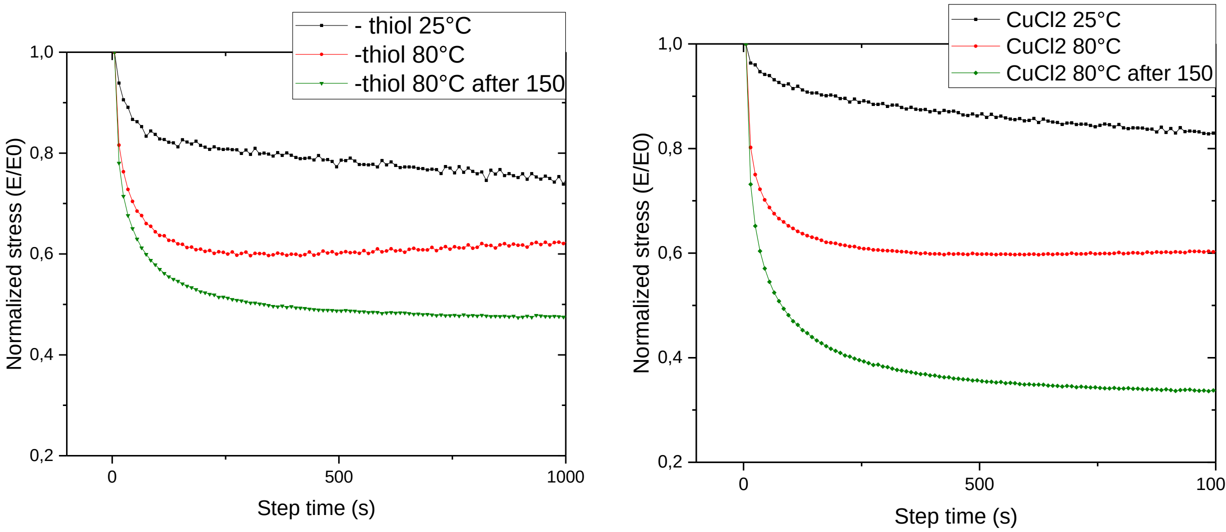


Figure 4-8 Stress relaxation graphs a)with and b) without copper chloride

When comparing the stress relaxation of all the three dual network epoxies (+ thiol, - thiol, + cucl2) , it is clear that the copper chloride mediated epoxy has the highest stress relaxation. This indicates that the presence of copper chloride does indicate accelerate the disulfide shuffling process.

The mechanism is most likely due to the formation of a disulfide complex (observed by a distinct green color of the polymer). The complex shows a distinct a small increase in mechanical properties which is most likely due ti the interaction between CuCl2 and S-S bonds leading to more closely bonded S-S bonds . Copper (II) chloride can thus be used as a catalyst to increase relaxation of the network by increasing disulfide reversibility.

4.3.3 Healing macroscopic damage

DCB samples with interlayer of the dual network epoxy with copper chloride were made and tested in Mode I opening using a double cantilever specimen. The load displacement curves are displayed in Figure 4-9. The black curve shows the pristine DCB sample. The pristine DCB sample shows initial resistance to crack growth, however the crack opens rapidly at strain 20mm and at 50mm. There was no crack healing observed at higher temperatures as shown by the red and blue curves when healed at 90°C and 130°C for 16 hours at 5 bar pressure.

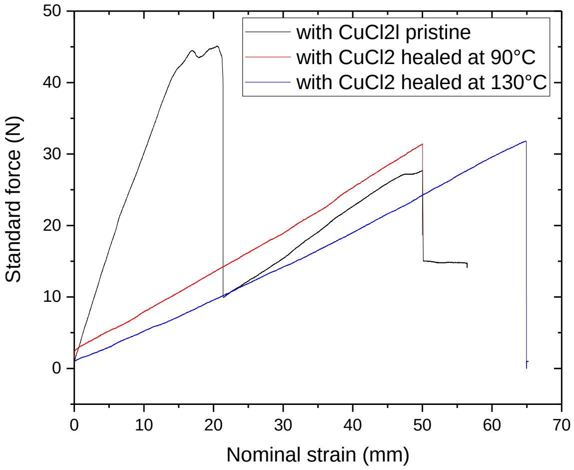


Figure 4-9 Load-displacement curves of dual network epoxy without thiol with copper chloride tested in mode I opening

The sudden crack opening in the black curve was observed to be delamination of the hybrid epoxy interlayer from the FRP surface. When the two halves were separated, there was complete absence of hybrid epoxy interlayer at two pints. This delamination behaviour was observed in all the three samples tested.

To understand the origin of delamination, a pristine sample which had not been tested was opened manually and the same delamination pattern as observed. While making the DCB interlayers, it was observed that the viscosity of the dual network epoxy increases due to the added copper chloride particles. However, the increased viscosity of the uncured hybrid epoxy possibly led to an interlayer of non-uniform thickness especially since the thickness of the interlayer is low (1mm). This non-uniform interlayer probably leads to regions with very low epoxy interlayer causing delamination

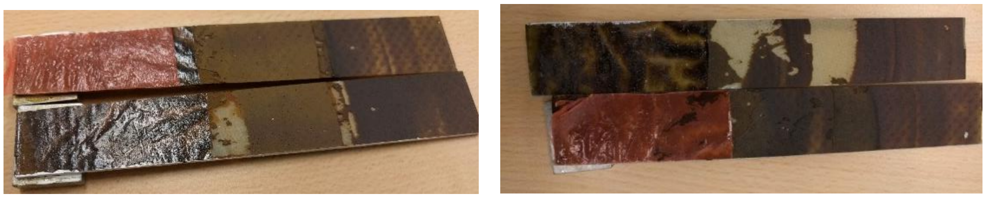


Figure 4-10: DCB sample with dual network epoxy containing copper chloride showing delamination from GFRP base a) Sample healed at 130°C b) Pristine sample opened manually

5 Inferences and Conclusions

Effect of thiol on dual network relaxation and healing

The role of tetra-thiol in a dual network disulfide-based epoxy developed for aerospace applications has been studied. Thiols have been studied in literature to assist disulfide healing by thiol-disulfide exchange reactions, however, their function in this system where there are both disulfides and epoxide groups has been unexplored.

Mechanical properties of the dual network epoxy decrease in the presence of thiol indicating the development of a less rigid network. Literature shows that in the presence of a strong base, thiols dissociate into thiolate ions at room temperature. These thiolate ions attack disulfides and epoxide groups leading to more S-S bonds and C-S bonds which are weaker than C-C bonds resulting in a weaker network in the presence of thiol. Thus, it is very likely that the thiol in the dual network epoxy participates in side reactions with disulfide and epoxide groups creating more S-S bonds and C-S bonds leading to a less rigid network.

Stress relaxation experiments at 80°C measuring the ability of the network to relax by reversible bond shuffling shows that the dual network epoxy without thiol has greater relaxation than the dual network epoxy with thiol, in spite of having a more rigid network.

Since there are no thiols to cause thiol-disulfide reactions in the dual network epoxy without thiol, the most likely mechanism for exchange reactions is thermally activated radical-mediated mechanism after sulfenyl radical creation by homolysis. This also then indicates that there is sufficient sulfenyl radical generation from the homolysis of disulfides at 80°C. This supports the Raman studies and other studies done in literature about the homolysis of disulfides.

Eliminating thiol, thus, increases stiffness & Tg of the dual network epoxy, while reducing relaxation time. However, it also reduced macroscopic healing behaviour of large scale damages created in mode I opening using DCB samples. This shows that thiols are not necessary for stress relaxation and that disulfide bonds can undergo reversible reactions aided by thermally generated radicals. However, for large-scale healing to take place, thiols play an important role in increasing the net S-S content and creating more macroscopic mobility.

This knowledge can thus be used to create disulfide-based epoxies which can relax in the absence of thiols by following thermally activated radical mediated exchange mechanism however maintaining high disulfide content along with a highly crosslinked flexible chain network. This can help create sufficient macroscopic reversibility without using thiols to possibly increase both the mechanical properties along with long term healing properties.

Effect of CuCl2 on thiol-free dual network relaxation and healing

The effect of using copper (II) chloride as a catalyst to promote disulphide homolysis was studied. Copper (II) chloride formed a dark green complex when mixed with disulfides. This dual network epoxy with CuCl2 exhibited a small increase in mechanical and thermal properties. This could possibly be due to the interaction between the S-S bonds and the CuCl2 when they form a Cu-S complex.

It was found that the addition of copper (II) chloride reduced the stress relaxation properties of the dual network epoxy without thiol at room temperature. However, at 80°C, the hybrid epoxy with copper chloride showed higher stress relaxation and faster kinetics than the hybrid epoxy without CuCl2.

The dual network epoxy with copper chloride however did not show any macroscopic healing. On closer inspection, it was found that the DCB samples showed delamination of the hybrid epoxy interlayer from the GFRP base. This could be due to the increased viscosity pf the uncured hybrid epoxy on mixing with copper chloride particles. Since a thin interlayer of 1mm was made, the higher viscosity of the hybrid epoxy could have led to uneven distribution of the interlayer causing delamination while testing.

Future work

A method has been established to understand the glass transition and reversible bond temperature along with a method to measure large scale macroscopic healing. Since the dual network epoxy without thiol and with CuCl2 show high relaxation and bond shuffling while showing relatively low large-scale damage healing, it is still possible that they show microscopic healing (<cm^2) which can be used to prevent micro-cracks in composites. Microscopic healing measurements by measuring recovery of fracture properties while doing low velocity impact tests can give more information on the healing of these dual networks.

Also more catalysts that can increase the disulfide exchange reactions can be explored. As mentioned before transition metal halides such as copper, cobalt, nickel and gold halides are interesting options to explore for disulfide homolysis due complex formation abilities that have been studied in the literature. Tests can be done to explore the reversibility of these complexes via stress relaxation. This can lead to a better understanding of the mechanism of healing via complex mediation.

Apart from this, now that there is a better understanding of how the various components in this system, the organic and inorganic networks interact and affect the properties, techniques to tweak the two architectures can be studied. A network architecture with high disulfide content can lead to sufficient macroscopic flow behaviour even in the absence of thiols. For eg. modifying the organic network by choosing a crosslinker that can have reversible disulfide linkages or by varying the inorganic to organic ratio, and choosing the architecture of the polymer carefully, properties of this disulfide-based epoxy can be further improved.

Bibliography

[1] S. Liu and J. A. Nairn, “Fracture Mechanics Analysis of Composite Microcracking: Experimental Results in Fatigue.”

[2] J. Dwyer-Lindgren, “How Boeing Will Fix Burned 787 Dreamliner - Business Insider,” 2013. [Online]. Available: https://www.businessinsider.com/how-boeing-will-fix-burned-787-dreamliner-2013-10?international=true&r=US&IR=T. [Accessed: 08-Aug-2018].

[3] M. Scheiner, T. J. Dickens, and O. Okoli, “Progress towards self-healing polymers for composite structural applications,” *Polym. (United Kingdom)*, vol. 83, pp. 260–282, 2016.

[4] K. Urdl, A. Kandelbauer, W. Kern, U. Müller, M. Thebault, and E. Zikulnig-Rusch, “Self-healing of densely crosslinked thermoset polymers—a critical review,” *Prog. Org. Coatings*, vol. 104, pp. 232–249, 2017.

[5] C. J. Kloxin and C. N. Bowman, “Covalent adaptable networks: smart, reconfigurable and responsive network systems,” *Chem. Soc. Rev.*, vol. 42, no. 17, pp. 7161–7173, 2013.

[6] A. V. Tobolsky, W. J. MacKnight, and M. Takahashi, “Relaxation of Disulfide and Tetrasulfide Polymers,” *J. Phys. Chem.*, vol. 68, no. 4, pp. 787–790, Apr. 1964.

[7] G. D. T. Owen, W. J. MacKnight, and A. V. Tobolsky, “Urethane Elastomers Containing Disulfide and Tetrasulfide Linkages,” *J. Phys. Chem.*, vol. 68, no. 4, pp. 784–786, Apr. 1964.

[8] X. Chen *et al.*, “A thermally re-mendable cross-linked polymeric material.,” *Science*, vol. 295, no. 5560, pp. 1698–702, Mar. 2002.

[9] † Xiangxu Chen, *,† Fred Wudl, ‡ Ajit K. Mal, § and Hongbin Shen, and S. R. Nutt§, “New Thermally Remendable Highly Cross-Linked Polymeric Materials,” 2003.

[10] T. S. Coope, D. H. Turkenburg, H. R. Fischer, R. Luterbacher, H. van Bracht, and I. P. Bond, “Novel Diels-Alder based self-healing epoxies for aerospace composites,” *Smart Mater. Struct.*, vol. 25, no. 8, p. 84010, 2016.

[11] D. H. Turkenburg and H. R. Fischer, “Diels-Alder based, thermo-reversible cross-linked epoxies for use in self-healing composites,” *Polymer (Guildf).*, vol. 79, pp. 187–194, 2015.

[12] R. Singh and G. M. Whitesides, “Thiol-disulfide interchange,” *Chem. Sulphur-Containing Funct. Groups*, pp. 633–658, 2010.

[13] I. Azcune and I. Odriozola, “Aromatic disulfide crosslinks in polymer systems: Self-healing, reprocessability, recyclability and more,” *Eur. Polym. J.*, vol. 84, pp. 147–160, 2016.

[14] F. Deè, M. Pichowicz, G. Povie, and P. Renaud, “Thiyl Radicals in Organic Synthesis.”

[15] I. V Koval ’, “The chemistry of disulfides,” *Russ. Chem. Rev.*, vol. 63, no. 9, pp. 735–750, 1994.

[16] S. Nevejans, N. Ballard, J. I. Miranda, B. Reck, and J. M. Asua, “The underlying mechanisms for self-healing of poly(disulfide)s,” *Phys. Chem. Chem. Phys.*, vol. 18, no. 39, pp. 27577–27583, 2016.

[17] A. Rekondo, R. Martin, A. Ruiz de Luzuriaga, G. Cabañero, H. J. Grande, and I. Odriozola, “Catalyst-free room-temperature self-healing elastomers based on aromatic disulfide

metathesis," *Mater. Horiz.*, vol. 1, no. 2, pp. 237–240, 2014.

[18] J. M. Matxain, J. M. Asua, and F. Ruipérez, "Design of new disulfide-based organic compounds for the improvement of self-healing materials," *Phys. Chem. Chem. Phys.*, vol. 18, no. 3, pp. 1758–1770, 2016.

[19] A. M. Grande, R. Martin, I. Odriozola, S. van der Zwaag, and S. J. Garcia, "Effect of the polymer structure on the viscoelastic and interfacial healing behaviour of poly(urea-urethane) networks containing aromatic disulphides," *Eur. Polym. J.*, vol. 97, no. October, pp. 120–128, 2017.

[20] M. Hernández, A. M. Grande, W. Dierkes, J. Bijleveld, S. van der Zwaag, and S. J. García, "Turning Vulcanized Natural Rubber into a Self-Healing Polymer: Effect of the Disulfide/Polysulfide Ratio," *ACS Sustain. Chem. Eng.*, vol. 4, no. 10, pp. 5776–5784, Oct. 2016.

[21] M. Abdolahzadeh, A. C. C. Esteves, S. Van Der Zwaag, and S. J. Garcia, "Healable dual organic-inorganic crosslinked sol-gel based polymers: Crosslinking density and tetrasulfide content effect," *J. Polym. Sci. Part A Polym. Chem.*, vol. 52, no. 14, pp. 1953–1961, 2014.

[22] M. Abdolah Zadeh, A. M. Grande, S. van der Zwaag, and S. J. Garcia, "Effect of curing on the mechanical and healing behaviour of a hybrid dual network: a time resolved evaluation," *RSC Adv.*, vol. 6, no. 94, pp. 91806–91814, 2016.

[23] W. Post, A. Cohades, V. Michaud, S. van der Zwaag, and S. J. Garcia, "Healing of a glass fibre reinforced composite with a disulphide containing organic-inorganic epoxy matrix," *Compos. Sci. Technol.*, vol. 152, pp. 85–93, 2017.

[24] M. C. Stuparu and A. Khan, "Sequential Thiol-Epoxy and Esterification Reactions: A Facile Route to Bifunctional Homopolymer Sequences," Springer, Cham, 2014, pp. 87–103.

[25] A. O. Konuray, X. Fernández-Francos, and X. Ramis, "Analysis of the reaction mechanism of the thiol–epoxy addition initiated by nucleophilic tertiary amines," *Polym. Chem.*, pp. 5934–5947, 2017.

[26] P. M. Boorman, K. A. Kerr, R. A. Kydd, K. J. Moynihan, and K. A. Valentine, "Synthetic, structural, and spectroscopic studies of the ligating properties of organic disulphides: X-ray structure of copper(I) iodide–diethyl disulphide (2/1)," *J. Chem. Soc., Dalt. Trans.*, no. 8, pp. 1401–1405, 1982.

[27] V. Subramanian and K. Seff, "Homolytic cleavage of the sulfur-sulfur bond in dimethyl disulfide by cobalt ions in partially cobalt(II)-exchanged zeolite A, Co4Na4-A," *J. Am. Chem. Soc.*, vol. 102, no. 6, pp. 1881–1884, Mar. 1980.

[28] N. Zhong and W. Post, "Self-repair of structural and functional composites with intrinsically self-healing polymer matrices: A review," *Compos. Part A Appl. Sci. Manuf.*, vol. 69, pp. 226–239, 2015.

[29] M. Hernández, A. M. Grande, W. Dierkes, J. Bijleveld, S. Van Der Zwaag, and S. J. García, "Turning Vulcanized Natural Rubber into a Self-Healing Polymer: Effect of the Disulfide/Polysulfide Ratio," *ACS Sustain. Chem. Eng.*, vol. 4, no. 10, pp. 5776–5784, 2016.

[30] L. H. (Leslie H. Sperling, *Introduction to physical polymer science*, 4th ed. Hoboken, N.J.: Wiley, 2006.

[31] H. P. Xiang, H. J. Qian, Z. Y. Lu, M. Z. Rong, and M. Q. Zhang, “Crack healing and reclaiming of vulcanized rubber by triggering the rearrangement of inherent sulfur crosslinked networks,” *Green Chem.*, vol. 17, no. 8, pp. 4315–4325, Aug. 2015.

[32] J. Canadell, H. Goossens, and B. Klumperman, “Self-healing materials based on disulfide links,” *Macromolecules*, vol. 44, no. 8, pp. 2536–2541, 2011.

[33] U. Lafont, H. Van Zeijl, and S. Van Der Zwaag, “Influence of cross-linkers on the cohesive and adhesive self-healing ability of polysulfide-based thermosets,” *ACS Appl. Mater. Interfaces*, vol. 4, no. 11, pp. 6280–6288, 2012.

[34] G. C. Tesoro and V. Sastri, “Reversible crosslinking in epoxy resins. I. Feasibility studies,” *J. Appl. Polym. Sci.*, vol. 39, no. 7, pp. 1425–1437, Apr. 1990.

[35] L. M. Johnson *et al.*, “Controlled degradation of disulfide-based epoxy thermosets for extreme environments,” *Polymer (Guildf).*, vol. 64, pp. 84–92, May 2015.

[36] A. Ruiz de Luzuriaga *et al.*, “Epoxy resin with exchangeable disulfide crosslinks to obtain reprocessable, repairable and recyclable fiber-reinforced thermoset composites,” *Mater. Horiz.*, vol. 3, no. 3, pp. 241–247, 2016.

[37] M. L. Henriksen, J. B. Ravnsbæk, M. Bjerring, T. Vosegaard, K. Daasbjerg, and M. Hinge, “Epoxy Matrices Modified by Green Additives for Recyclable Materials,” *ChemSusChem*, vol. 10, no. 14, pp. 2936–2944, 2017.

[38] J. Mijovic and J. Wijaya, “Etherification reaction in epoxy-amine systems at high temperature,” *Polymer (Guildf).*, vol. 35, no. 12, pp. 2683–2686, 1994.

[39] L. Xu and J. R. Schlup, “Etherification versus amine addition during epoxy resin/amine cure: An in situ study using near-infrared spectroscopy,” *J. Appl. Polym. Sci.*, vol. 67, no. 5, pp. 895–901, Jan. 1998.

Appendix A

Modifying organic network of dual network epoxy

Disulfide scission and exchange in polymers was first observed by Tobolsky et al in 1964 when they studied the stress decay and creep in polymers containing disulfides and tetrasulfides [6], [7]. Even though this knowledge was known more than 50 years ago, disulfide exchange was mostly considered an unwanted reaction causing creep in natural rubber Their potential for creating reversible thermosetting polymers and specifically epoxies has only gained huge momentum in the past decade.

Through the past decade various approaches have been tried to incorporate disulfides within the epoxy network. This section describes some of the modification to the organic network that were studied and tested. As mentioned before, one of the ways of increasing healing efficiency is to increase the reversible bond content by incorporating disulphide bonds into the epoxy or amine cross-linker.

Epoxy monomer with disulfides

Canadell et al [32] first studied the healing ability of disulfide containing networks by crosslinking EPS 25 with pentaerythritol tetrakis(3-mercaptopropionate) as shown in Fig 4. The resulting material was a transparent thermoset rubber that had a Tg about -35°C. This material showed healing ability at 60°C and the healing was attributed to disulfide exchange by comparison to a control.

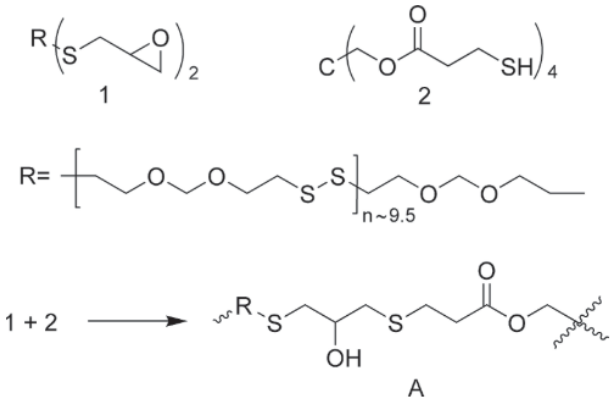


Figure A-1 Chemical structure of EPS shown by compound 1 and tetrathiol shown by compound 2. A- represents the cured epoxy network [32]

This system was further studied by Lafont et al [33] where they confirm the mechanism of healing in this system. The absence of pending thiols and the ability to recover properties for at least 10 cycles show that the healing is primarily due to disulfide opening and exchange.

Also, the crosslinker was varied to see its effect on the mechanical and healing properties. Pentaerythritol tetrakis(3-mercaptopropionate) (tetrathiol) was replaced with Capcure 3−800 which has three thiols per cross-linker unit as shown in Fig 5. The effect of reducing the crosslinking density not only reduced the mechanical properties but also the healing efficiency. It was found that, for a network that contains flexible chains and at low temperatures, a dense network formed from tetrathiol had better healing properties due to the easier access to disulfide bonds to shuffle. Giving more energy to the system by increasing the healing temperature minimizes the negative effect of the network cross-link density as well as the negative effect of chain rigidity on the healing rate. [33]

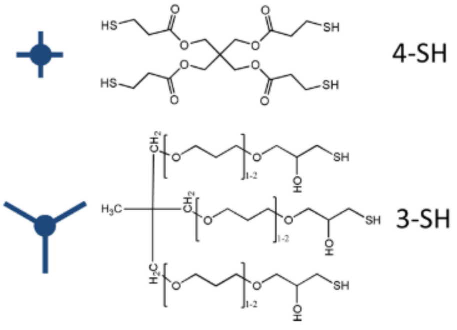


Figure A-2 Chemical structure of Pentaerythritol tetrakis(3-mercaptopropionate) (tetrathiol)- 4SH and Capcure 3–800 - 3SH [33]

One of the main problems of using EPS 25 is the relatively low strength of the monomer when compare dot commercial epoxy DGEBA. This can be seen in the differences between the Tg of EPS 25 crosslinked with tetrathiol which is -45°C compared to DGEBA crosslinked with the same tetrathiol which is 55°C. That is a huge 90°C difference in Tg which makes the former an elastomer at room temperature and the latter a stiff thermoset at room temperature. Even EPS 70 which has aromatic rings in its monomer structure when compared to the aliphatic chains in EPS 25 is not a huge improvement as the Tg of EPS 70 crosslinked with tetrathiol is about -4°C.

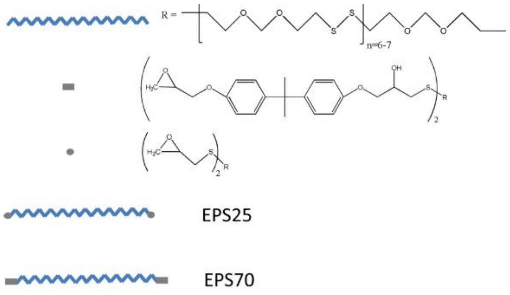


Figure A-3 Chemical structure of EPS 25 and EPS 70 [33]

Crosslinker with disulfides

Tesoro et al in 1990 [34] did the first feasibility studies to incorporate disulfide bonds in epoxy networks by trying different types of disulfide containing crosslinkers They crosslinked Epon 828 with dihydrazides of dithiodicarboxylic acids (aliphatic and aromatic) and dithio-aromatic diamines. They found that epoxy cured with disulfide containing aromatic diamine (4-aminophenyl disulfide) had the ability to show cleavage and reformation of disulfide bonds.

Johnson et al in 2015 used Bisphenol-F diglycidyl ether and 4-aminophenyl disulfide based on the work of Tesoro et al to create thermosets that can be degraded in a controlled manner [35]. The goal of their study was not to create self-healing thermosets but instead create materials for oil exploration and production which requires the materials to withstand harsh conditions and yet be able to degrade when required using specific chemicals. The resulting material had a Tg of 130°C and could withstand conditions of two weeks, 69MPa, 100 °C, pH 12. However, they were completely soluble in 2-mercaptoethanol due to the thiol disulfide exchange reactions.

In 2016, Odriozola [36] et al used the same monomers as Tesoro et al, diglycidyl ether of bisphenol A and 4-aminophenyl disulfide to study the healing properties of the resulting network. The chemical structures of the monomers and the resulting network is shown in the Fig. 15.

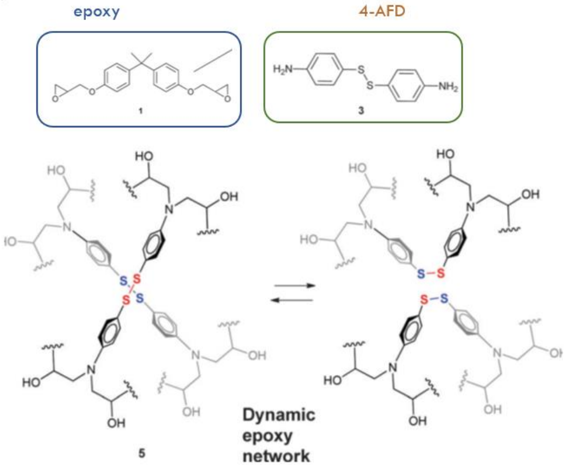


Figure A-4 Chemical structures of the DGEBA and 4 AFD and the resulting dynamic network [36]

They found this material to have very high strength (Stress at break of about 80MPa with 7% as the strain % at break) and yet be completely reprocessable at 200°C and 100 bar pressure. Since this material does not have any thiols or any catalyst that can lead to thiolate ions, it can be assumed that the healing and reshaping ability stems from disulfide homolysis and radical exchange reactions. Stress relaxation experiments done on this material shows that it has very fast relaxation times ranging from 3 hours at 130°C to 20 seconds at 200°C in spite of having a very high Tg of 130°C.

Even though this material is very promising, it faces a few problems for large scale use a s a matrix in composites. First, it is extremely stiff and has very low toughness and hence prone to impact damage. Moreover, the healing happens at very high temperature and pressure (200°C and 100 bar) which makes it very difficult to heal on a large scale when used in composites. The monomer 4AFD is also very expensive.

Most of the literature is focused on 4AFD as it undergoes spontaneous homolysis at room temperature. This is because electron donating groups, specifically NH_2 coupled with aromatic ring leads to delocalization of the unpaired electron of the radical generated and stabilization which reduces the bond dissociation energy of the S-S. Hence, 4AFD is a very good candidate for future research as matrix material for aerospace composites, if it can be modified to be less expensive and when used in conjunction with other chain extenders that can increase toughness of the material.

Chain extender with disulfides

Henriksen et al [37] studied the use of different crosslinkers and chain extenders in standard epoxies to make them recyclable. Their goal was to make these epoxies recyclable by making them susceptible to fractionating by DMF, acetic acid etc. They used 2- hydroxyethyl disulfide as a chain extender along with commercial epoxy amine monomers.

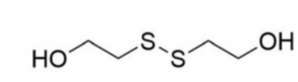


Figure A-5 Chemical structure of 2- hydroxyethyl disulfide

However, one of the major problems of using alcohols to react with epoxy groups in the presence of amines is the relatively low reactivity of alcohols. The reaction between an epoxy group and alcohol is known as an etherification reaction. Etherification reaction is generally non-existent in the presence of epoxy amine reaction. This is because even though amines and alcohols have the same mechanism of reaction with epoxies as shown in the Fig 20, amino groups have much higher nucleophilicity when compared to hydroxyl groups to open the epoxy ring. This reaction is only favoured at high temperatures or at epoxy: amine ratios >1. Even with this high temperature and stoichiometry, this reaction is 10-15 times slower than epoxy amine reaction. [38][39]

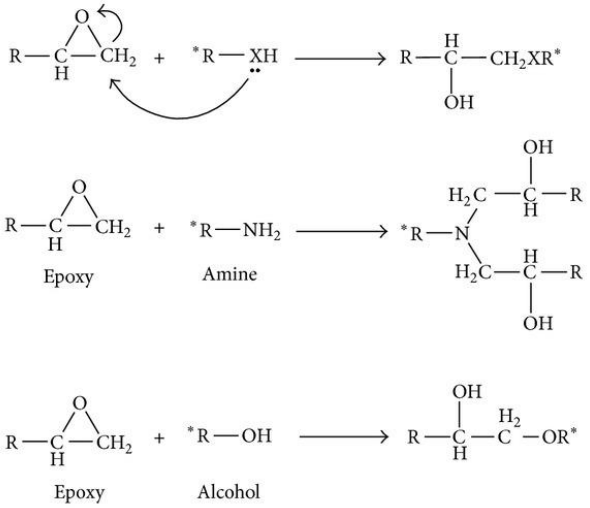


Figure A-6: Mechanism of epoxy- amine and epoxy- alcohol reactions

At higher temperatures, chain extenders like 2- hydroxyethyl disulfide prove to be very toxic as it has a boiling point of 150°C and being a small monomer unit with disulfides, the vapors are extremely toxic. This proves as a challenge to include it as a good chain extender as it limits curing temperatures and healing temperatures

.

Appendix B

Possible explanations for greater stress relaxation in the absence of thiol in the dual network epoxy

The greater relaxation of the dual network epoxy without thiol when compared to the dual network with thiol is interesting to explore further. Given that the stress relaxation tests were performed at 80°C which is very close to the beginning of the glass transition, the polymer chains probably have some limited molecular motion. It is very likely that at this temperature the stress relaxation *is highly dependent on the proximity of the disulfide bonds due to the limited chain mobility of the networks*.

In such a case it could be that the absence of thiol leads to a more closely spaced network making it easier for the sulfenyl radicals to shuffle without having to move much. This could explain the reason as to why in spite of the fact that the network is less mobile and probably has lesser disulfides due to the absence of thiol it still has higher bond shuffling kinetics.

In order to test this hypothesis to see if the absence of thiol leads to a more denser network and hence faster relaxation, the density of both dual network epoxies were measured. Archimedes principle was used to measure densities of both hybrid epoxies and they are as shown below:

Density of dual network epoxy with thiol: 1.24g/cm3

Density of dual network epoxy without thiol: 1.14g/cm3

Density of hybrid epoxy with thiol is higher than that without thiol which could be due to the higher density of tetrathiol (1.28 g/ml) when compared to the density of Ancamine (1.07g/ml) which could be a reason why the epoxy which had thiol had higher density. Thus, this does not yet explain the higher stress relaxation in the dual network without thiol.

Since the temperature sweeps of both hybrid epoxies in DMA show comparable storage modulus, with the dual network epoxy without thiol showing a slightly higher E' at room temperature, it is likely that both networks have comparable crosslinking densities.

It could be that the thiol in some way increases the distance between the S-S bonds in spite of comparable crosslinking density. Since thiols react with the disulfide in the inorganic network and the epoxide rings in the organic network, it probably acts as a cross linker between the two networks. In the absence of thiols, only APS acts as the crosslinker between the organic and inorganic networks

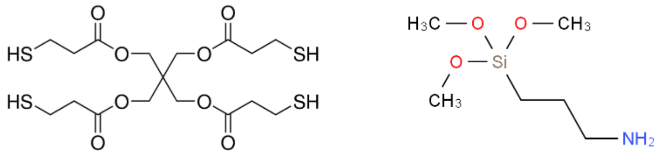


Figure B-1 Chemical structures of tetrathiol and APS

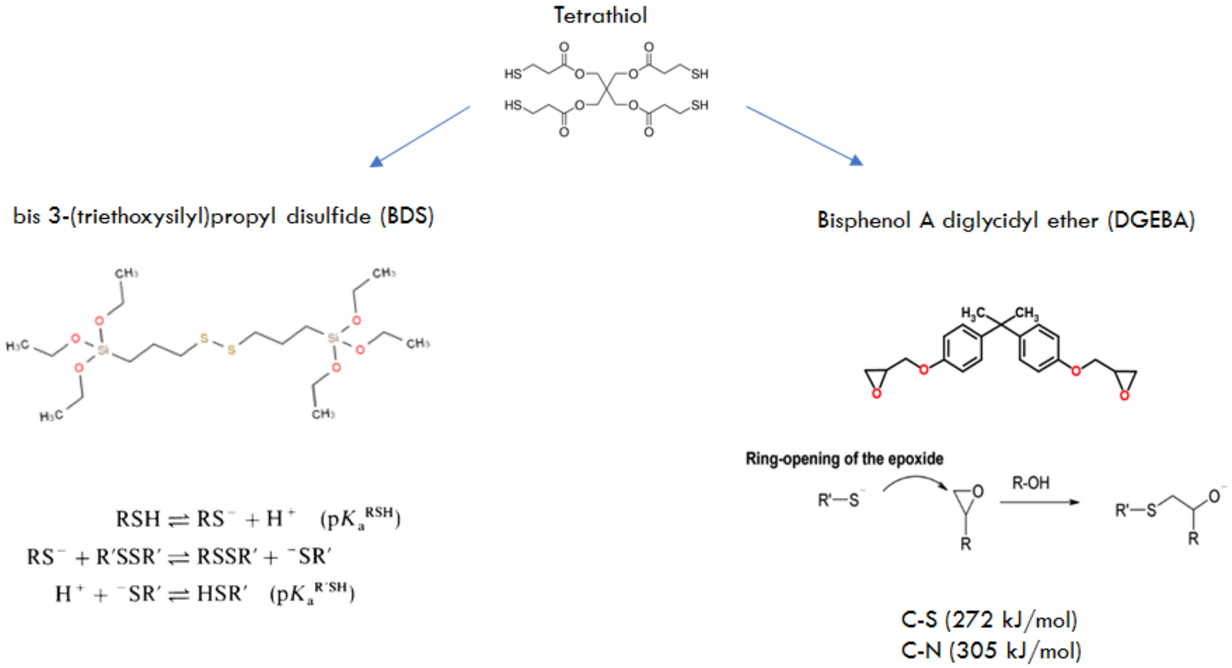


Figure B-2 Thiol reacts with both inorganic and organic components and could acts as a cross linker between the two

The epoxy network is non reversible and probably acts as a block between disulfide bonds. This reaction of tetrathiol as a crosslinker could lead to more organic inorganic crosslinks separating the reversible S-S bonds. Also the tetrathiol molecule is bigger than the Aps molecule possibly leading to more widely spaced crosslinks. These problems can be avoided by eliminating thiol and increasing the S-S content of the network by using organic monomers with S-S. Further work needs to be done to understand the origin of this difference in relaxation behavior and their effect on the macroscopic healing.

.