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UNIVERSITY OF CALIFORNIA,
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Chemically-degradable Epoxy Networks Designs via Dynamic Covalent Chemistry

THESIS

submitted in partial satisfaction of the requirements
for the degree of

MASTER OF SCIENCE

in Chemical and Biomolecular Engineering

by

Pei-Ting (Peggy) Chung

Thesis Committee:
Professor Zhibin Guan, Chair
Assistant Professor Herdeline Ann Ardoña
Assistant Professor Seunghyun Sim

2023

DEDICATION

To

my parents and friends

in recognition of their worth

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ABSTRACT OF THE THESIS

Chemically-degradable Epoxy Networks Designs via Dynamic Covalent Chemistry

by

Pei-Ting (Peggy) Chung

Master of Science in Chemical and Biomolecular Engineering

University of California, Irvine, 2023

Professor Zhibin Guan, Chair

A method for incorporating dynamic covalent bond into epoxy networks has been developed using a siloxane exchange pathway with the help of a fluoride catalyst, CsF. It has been demonstrated that the siloxane-based epoxy network containing catalytic amounts of CsF exhibits dynamic behavior, allowing for the exchange of cross-linked bonds within a useful temperature range of 160 °C to 200 °C. This pathway exhibits a lower activation energy and improved thermal stability compared to the same siloxane-based epoxy network catalyzed by 1,5,7-triazabicyclo [4.4.0] dec-5-ene (TBD) as an organic catalyst. Furthermore, the CsF-catalyzed polymer has been shown to maintain the same stress-relaxation rate and crosslinked density after being reprocessed up to five times.

CHAPTER 1: Introduction to Chemically-Exchangeable Bonds in Polymer Networks

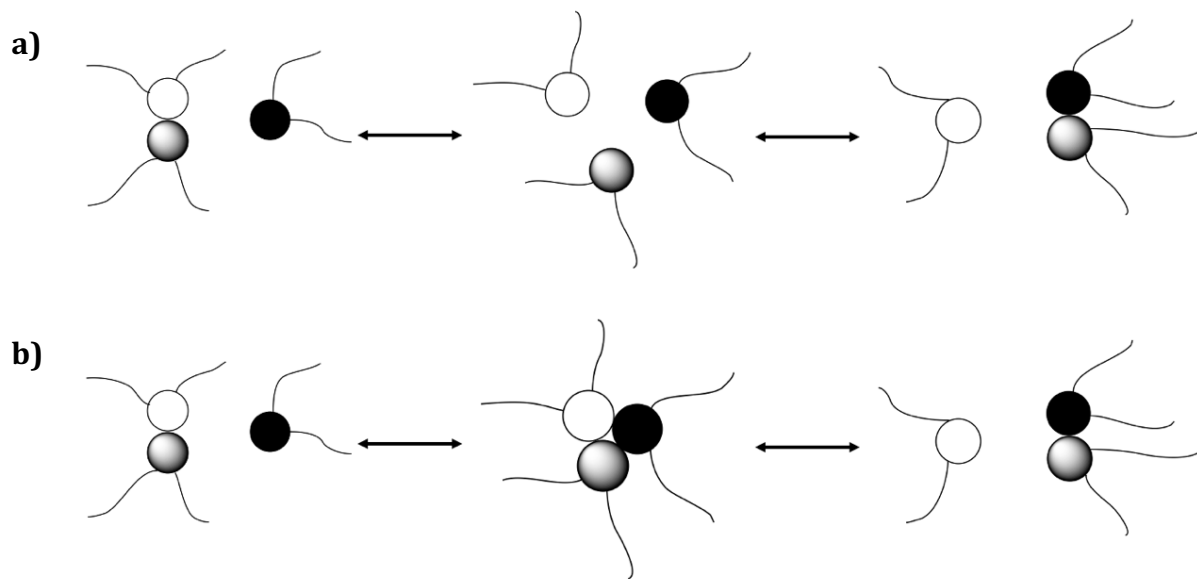
1.1 The Background of Dissociative/Associative Dynamic Covalent Chemistry in Polymers

Synthetic polymers are man-made macromolecules composed of repeated structural units called monomers. Thermoplastics are one type of such polymer; they can be repeatedly molded into various shapes under high temperatures and solidified when cooled.¹ Thermoplastics are widely used polymers and include polyvinyl chloride, polyethylene, and polymethyl methacrylate. They are popular because they can be reprocessed, and this increases their utility in day-to-day life.² These polymers are used to make bottles, shopping bags, textiles, fibers, and water pipes. Thermoplastics differ from another category of plastics called thermosets. Thermosets undergo a chemical reaction during a curing process which confers them permanent network structure and unique properties such as chemical and creep resistance. The chemical structure and bonding of thermosets make them thermally stable and resistant to deformation under load.³ Examples of thermosets are epoxy resins, phenolic resins, polyurethane resins, and unsaturated polyester resins. They are used to make adhesives, coating, electrical molding, car parts, and furniture. In this work, my aim is to assess the current trends in improving polymers to produce high-quality materials.

Dynamic covalent chemistry (DCC) is a branch of chemistry that deals with the formation of reversible covalent bonds. The bonds are unique in that they form and break under a specific stimulus such as temperature or pH change.⁴⁻⁶ The same cannot be said about traditional covalent bonds, which are strong and stable. Some common examples of

available DCC include imine exchange,⁷ amination exchange,^{8,9} boronic acid exchange,^{10,11} Diels-Alder cycloadditions,^{12,13} alkene and alkyne metathesis,¹⁴⁻¹⁸ transesterification,¹⁹⁻²¹ disulfide exchange,²² silyl ether exchange,²³ reversible addition-fragmentation radical chemistry,²⁴⁻²⁷ and many others.²⁸ When used in the formation of polymers, they can thus exhibit characteristics similar to thermoplastics, such as allowing reproducibility under high temperatures while at room temperature behaving like thermosets by providing strength, solvent resistance, and creep resistance.

For DCC to have a practical role in the formation of polymers, two requirements must be met: reversibility and stability. The chemical reaction involved in the dynamic bond must remain completely reversible.²⁹ One manner that this can be achieved is through the use of specific catalysts, which lower the activation energy making certain reactions reversible.³⁰ It is also essential that the formed material has thermal stability and cannot deform under load. Brittle plastics are made malleable by applying heat, which manipulates the dynamic chemical bond. This converts the DCC into dynamic thermosets.



Scheme 1 Dynamic covalent chemical cross-linker exchange pathway by using an a) dissociative exchange mechanism and b) associative exchange mechanism.

When used to make polymers, DCC is largely classified into dissociative exchange and associative exchange in reference to the mechanism of reversible formation and cleavage.³¹ A dissociative exchange first involves the dissociation of a bond before the substitution can occur. In associative exchange, there is an initial formation of an intermediate before the breaking of a bond. In situations where structural changes are required, the dissociative exchange mechanism is the desired mechanism of polymer formation. This is because, at extremely raised temperatures, the equilibrium of DCC shifts towards the reactants and results in the system flowing like a molten liquid.⁴

In many circumstances, maintaining the network integrity intact at extremely high temperatures is preferred to melting. Associative exchange, by virtue of forming an intermediate, enables a gradual change in viscosity as a function of temperature, these

polymers are called vitrimer. In other words, associative exchange leads to a constant crosslink density, despite its dynamic nature. Because the system is crosslinked, the polymer cannot melt. Yet, it still remains adaptable when subjected to external pressures. The rate at which this exchange occurs is often temperature-dependent. Such networks are unique because they can exchange their crosslinks through an associative mechanism mainly triggered by heat. As typical of classical thermosets, these products are insoluble in organic solvents.

In conclusion, the need for malleability while maintaining thermal stability has led to increased studies and research in the field of polymer chemistry. The attention has shifted to vitrimers that possess both thermosets and thermoplastic characteristics. Access to such systems with chemically inert motifs and good reprocessability welcomes a more sustainable future for plastic materials.

1.2 Epoxy Networks and their Applications/Shortcomings

Epoxy networks are polymer networks formed as the result of an epoxy prepolymer reacting with a hardener which (typically a diamine or triamine) crosslinks the chains together.³² The ring-opening of epoxides, as well as the high tensile strength, are some characteristics that distinguish epoxy resins from other types of polymers, such as addition polymers like polyethylene or polypropylene, which grow through repetitive addition reactions of monomers.

The origins of epoxy resins can be traced back to the early years of the 20th century when in the 1930s, Pierre Castan, a Swiss chemist, discovered the reaction between epichlorohydrin and bisphenol-A, resulting in the formation of a thermosetting resin with a three-dimensional network structure. Further advancements in epoxy resins came in the 1940s when Sylvan Greenlee, an American chemist, improved the synthesis and developed methods to commercialize epoxy resins. During this time, World War II was still going on, and epoxy resins gained significant attention due to their excellent adhesive properties and were used for various military applications. After the war ended and the years progressed, epoxy resins became more popular and are now widely used across various domestically at home and in industries, namely: aerospace, construction, electronics, and automotive, and have thus been adopted widely for use across all sectors of life.

Epoxy networks, almost a hundred years later since their discovery, have changed the lives of millions of people globally through their multiple applications and uses worldwide in different sectors of the economy and industry. People have been using them in their daily lives at domestic and industrial levels; epoxy resins have found use as certain types of glass alternatives, flooring, as well as an adhesive for binding components together. Based on these reasons, over the years, they have been noted to be especially significant in the following ways, which well describe their commonly recognized qualities and attributes:

To begin with, epoxy networks are known for their outstanding mechanical properties, including strength and durability. They possess high tensile and compressive

strength, toughness, and resistance to impact, making them ideal for load-bearing applications and guaranteeing long-lasting performance³².

Secondly, they are highly resistant to chemicals, solvents, and environmental factors like moisture, UV radiation, and temperature fluctuations. Materials made from these resins maintain these good qualities even if the final products made are not necessarily epoxy resins.³³

Lastly, epoxy networks can be tailored to specific requirements by modifying the resin formulation, curing agents, or additives. This versatility enables their application in a wide range of industries and allows for the development of custom materials with desired properties³².

Over the years, research and development efforts have led to the formulation of epoxy resins with improved properties, including enhanced mechanical strength, chemical resistance, and flexibility. Today, epoxy resins are widely used across industries and have become an essential material for a variety of applications ranging from adhesives and coatings to composites and electronics.³⁴ They have notably found their significance in the following key applications and products:

The most commonly used application product of epoxy resins is adhesives. Epoxy adhesives are widely used for bonding various materials, including metals, plastics, ceramics, and composites. According to Schulenburg, J.O., & Kramer, "Polyurethane or epoxy-based structural foams contribute to both structure stiffness and crash resistance and allow novel lightweight constructions."³⁵ This is an example of a commonly used resin in the motor industry which clearly now shows how they provide high strength and

excellent adhesion properties, making them ideal for applications such as construction, automotive manufacturing, and even in electronic assembly.

Coatings and paints are another real-life use of these resins. Most houses in the neighborhood have some paints of different colors painted on them. Some of these are made from these resins. Epoxy-based paints are commonly used for corrosion protection on metal surfaces, floor coatings, and as decorative finishes in houses, offices, or whenever they are required.³⁶ Epoxy coatings can also be found on countertops, appliances, and other household items.

Epoxy resins also find wide applications in the electronics industry for encapsulating and potting electronic components, such as circuit boards, transformers, and sensors.³⁷ Their excellent insulating properties help protect delicate electronic systems from moisture, dust, and mechanical stress from any eventual damage that could come from the environment.

Lastly, epoxy network products also find applications in manufacturing composite materials. Epoxy resins are a vital component in the manufacture of composite materials, such as carbon fiber-reinforced polymers (CFRP).³⁷ The high strength, stiffness, and resistance to chemicals and heat make epoxy-based composites suitable for aerospace, automotive, sports equipment, and construction applications.

Although epoxy networks have a wide range of applications, there are still some limitations that need to be addressed:

One limitation that is easily noted in epoxy resin products is their brittleness³². They can be relatively brittle, especially when used in thick sections or exposed to low

temperatures. This brittleness can result in reduced impact resistance and susceptibility to cracking or chipping under certain conditions.

Secondly, considering the UV degradation, epoxy networks are prone to degradation when exposed to prolonged UV radiation.³⁸ Over time, the material may turn yellow, lose gloss, or experience surface degradation. However, this issue can be mitigated by incorporating UV stabilizers or applying protective topcoats.

Thirdly, there is a lack of both toughness and flexibility.³⁹ While epoxy networks offer high strength and rigidity, they may lack the toughness and flexibility needed for specific applications. In situations requiring materials with enhanced impact resistance or elongation capabilities, alternative polymers or elastomers might be preferred.

Curing shrinkage is another disadvantage of these epoxy networks,⁴⁰ and this particular disadvantage usually affects the production of the final product. It can be noted that during the curing process, epoxy networks undergo shrinkage as they transition from a liquid to a solid state. This shrinkage can lead to internal stresses and the development of micro-cracks, potentially impacting the mechanical integrity of the material, which could later turn out to be risky when used in other.⁴¹

Epoxy networks can absorb moisture from the environment, which can negatively affect their performance and properties.⁴² Moisture absorption can lead to reduced mechanical strength, dimensional changes, and decreased adhesion to substrates.

The most sensitive and concerning limitation of epoxy networks is how they affect health and safety and how they should be disposed of. The handling, processing use, and disposal of epoxy resins sometimes typically involve the use of curing agents and solvents,

which can release volatile organic compounds (VOCs) and pose health risks. For example, James Griffin explains that disposing of epoxy resins presents a common problem as the epoxy itself is typically a flammable liquid, while the hardener or curative, though non-flammable, may be corrosive or toxic.⁴³ Proper ventilation and personal protective equipment (PPE) are necessary to ensure safety during epoxy application. These guidelines typically involve segregating the epoxy resin and hardener components, allowing them to cure separately, and then disposing of them as prescribed by local regulations for hazardous waste.

1.3 Recyclability of Epoxy Networks

To begin with, it is important to note that epoxy resin recycling is a complex and evolving field, and there is ongoing research to develop more efficient and sustainable recycling methods. While epoxy networks are known for their excellent properties, their recyclability can be challenging due to their cross-linked structure, which hinders the breakdown of the resin. However, researchers and industries are actively exploring various methods to enhance the recyclability of epoxy networks.

Smith reported that the majority (76%) of synthetic polymers produced in the United States are made up of six specific compounds known as the "Big Six". Each polymer is assigned a recycling code from 1-6 to indicate its recyclability, with lower numbers indicating easier recycling.³² The remaining 24% of synthetic polymers fall into different groups, including epoxy resins. Epoxy resins are a type of thermosetting polymer that

contain -C-O-C- groups in their structure. Unfortunately, these materials are not commonly recycled due to their recycling code of 7 and their cross-linked structure, which typically results in degradation rather than softening (preventing reshaping).

In the scale mentioned above, epoxy resins, being thermosetting plastics, have different properties and recycling considerations compared to these other common synthetic polymers. This is because they require specialized recycling processes and facilities, and as such, they are usually not assigned recycling codes within the 1-6 range. Instead, they are often categorized under recycling code 7 (Other Plastics) or may have specific recycling instructions provided by the manufacturers.

Although they transform lives daily, the disposal of epoxy resins remains a huge challenge, and this is a direct threat with regard to the commitments made toward environmental sustainability.

The following are examples of epoxy-based products that are capable of being recycled:

One way that can be used is the method of thermal degradation of the used epoxy resin.⁴⁴ One potential example could be the recycling of epoxy-based composite materials used in the automotive and aerospace industries. These composites often consist of epoxy resins reinforced with fibers like carbon or glass. Through controlled thermal degradation, the composite can be subjected to high temperatures to break down the epoxy resin, separating it from the reinforcing fibers. Using this method, it is possible, therefore, to recycle used epoxy networks and resins because the resulting depolymerized fibers and epoxy can be further processed and potentially reused in the manufacturing of new

composite materials or other epoxy-based products.⁴⁵ For thermal degradation, it's worth noting that the decomposition of epoxy resins may produce fumes, gases, or residues that can be hazardous or unpleasant. Therefore, it's important to handle and dispose of epoxy resins properly and follow appropriate safety guidelines when working with them at elevated temperatures or during all recycling processes.

Chemical recycling could also be a solution to the recycling of epoxy networks. An example of chemical recycling could be the depolymerization and recycling of epoxy-based adhesives, paints, and even electronic components, such as circuit boards. In this regard, epoxy-based coating like polyethylene terephthalate (PET)--based epoxy resin can be glycolyzed and recycled.⁴⁶ According to Bal et al., “chemical recycling methods such as glycolysis, hydrolysis, aminolysis, hydrolysis-glycolysis have also gained importance over the years”.³³ For example, paint-based epoxy resin adhesives or electronic circuit boards often contain epoxy resins as an insulating material. Chemical solvents or processes like the ones described above can be employed to dissolve or depolymerize epoxy resin selectively. For instance, for the electronic circuits, the electronic components can be separated from materials present on the board, and then the depolymerized epoxy can undergo further purification and potentially be reused in the production of new electronic components or other epoxy-based products.

The use of environmentally friendly recycling methods like bio-recycling could also be one of the best methods. This method offers the lowest impact on the environment. This is because it is bio-friendly, and as long as the material that is placed to biodegrade is placed in favorable conditions to enable this process, it will eventually work. According to

Smith, "Another solution to the accumulation of waste polymers in landfills is to design and use polymers that are biodegradable".³² The recycling of epoxy network products during processing can ease everything via aminolysis, which is a reaction in which an amine compound reacts with another compound, typically an ester or a carbonyl compound, to form a new product. One way to increase the biodegradability of cured epoxy material is to use bio-based or biodegradable amine compounds as curing agents. Another method is to modify the epoxy resin structure by adding biodegradable additives or reactive sites for biodegradation. These changes can have an impact on the final product's biodegradability.

I have discussed the importance of dynamic covalent chemistry, indicated two different pathways of the dynamic covalent chemical cross-linker exchanging, and included vitrimer in the previous section. It is worth noticing that vitrimers, which have both thermosets and thermoplastic characteristics, are getting more attention. When it comes to the creation of plastic materials that are sustainable and can be repeatedly used, vitrimer is a highly recommended option. However, it's important to take into account both the advantages and disadvantages that come with using epoxy networks. Though they provide excellent mechanical properties, solvent resistance, and versatility, these networks can also be inflexible, brittle, and prone to moisture sensitivity. Despite these drawbacks, epoxy networks are still extensively used in the manufacturing of adhesives, paints, electronic components, and many other products, owing to their outstanding properties. Although epoxy networks have excellent properties due to their cross-linked structure, they are challenging to recycle. To make dynamic polymer networks more widely used, they must possess good mechanical properties, stability in processing conditions, and resistance to

the common atmosphere. Our lab is dedicated to developing dynamic linkages that meet these criteria to the best of our ability.

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CHAPTER 2: Epoxy Networks Bearing Dynamic Siloxane Motifs

2.1 Introduction

Accumulation of plastic waste in the environment is a global crisis that needs an urgent response, one which should be informed by material synthesis and design. One such field for improvement is in the formation of epoxy networks, which are ubiquitous thermosetting material that cannot be reshaped once cured. Previous efforts to make epoxy networks more sustainable include Zhao et al.¹, Ocando et al.², and Debsharma et al.³ The latter of these proposed solutions involves the creation of crosslinked materials that are both mechanically stable, yet can still be reprocessed/recycled.^{4,5} These non-permanently crosslinked networks, called “vitrimers,” are a novel family of polymeric materials that possess excellent dynamic crosslinks that undergo exchange reactions with one another under heat and stress^{4,5}. Further, vitrimers have an associative mechanism that retains crosslinking density and prevents network integrity compromise even at elevated temperatures.^{6,7} Hence, vitrimers have found numerous applicability in areas that require dimensional stability, increased solvent resistance, and temperature-induced creep resistance.⁸ In this regard, numerous vitrimer motifs have been explored, encompassing transamination of vinylogous urethanes,⁹⁻¹³ boronic ester or boroxine exchange,¹⁴⁻¹⁹ imine exchange,²⁰⁻²³ transition metal-catalyzed transesterification,²⁴⁻²⁷ olefin metathesis,²⁸ triazolium trans-alkylation,²⁹ acetal exchange,^{30,31} siloxane exchange,^{32,33} and thiol conjugate addition-elimination.³⁴ However, though pioneering and extensively explored, these motifs showcase numerous limitations, such as oxidative, thermal, and hydrolytic stability issues or challenges in their syntheses. Correspondingly, these limitations have hampered the usability of vitrimers in commercial applications. The current proposal seeks

to find a way to minimize the said limitations to encourage the use of vitrimers in an industrial setting.

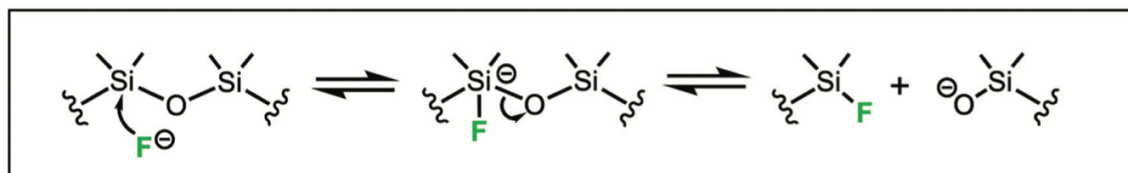
Debsharma³ and Tretbar³⁵ have conducted studies on dynamic networks involving siloxane crosslinkers and different catalysts. As stated by Debsharma³, their research has led to the creation of epoxy resins that possess the unique ability to be reshaped and reprocessed numerous times given particular conditions. Moreover, these resins exhibit remarkable relaxation properties, taking no more than 10 seconds to do so, with a derived activation energy of 87 ± 1 kJ/mol.³ They found that organic catalysts such as 1,5,7-triazabicyclo [4.4.0]dec-5-ene (TBD) can accelerate the siloxane exchange rate to create the desired new vitrimer. Vitrimers have unique properties that make them ideal for industries like aerospace, automotive, and biomedical. They can be reshaped and recycled multiple times, making industrial processes more sustainable and cost-effective.

The article by Tretbar et al.³⁵ similarly talks of vitrimers as materials that have advanced physical and chemical characteristics but are also capable of maintaining reprocessability. The vitrimers are, however, limited to specific polymers for them to meet the desired characteristics. As such, the article points out that F-catalyzed Siloxanes are often preferable over others as they are not only readily accessible chemical motifs but are also more stable to heat and higher temperatures, oxidation, and hydrolysis.

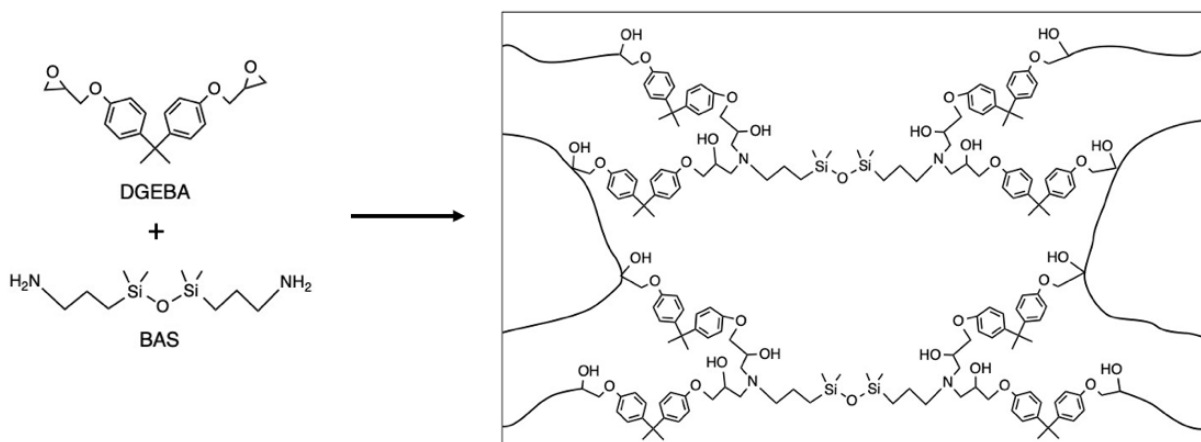
2.2 Results and Discussion

The underlying siloxane exchange mechanism was analyzed thoroughly by the researchers in order to develop a dynamic material with rapid dynamic exchange and siloxane content. In my previous attempt, I discovered that epoxy networks containing siloxane do not exhibit dynamic exchange behavior unless a catalyst is present. The preceding section delved into the concept that in the presence of a fluoride catalyst, a siloxanolate intermediate has the potential to interact with a silyl fluoride species from a distinct siloxane linkage, resulting in the formation of a fresh siloxane bond will be used in this research. This mechanism simultaneously revitalizes the fluoride catalyst.

Furthermore, the siloxanolate intermediate can directly target a neighboring siloxane linkage (Scheme 2.1). Since the F^- -catalyzed pathway shows higher stability and lower activation energy than the TBD-catalyzed pathway, I decided to incorporate the F^- catalyst into epoxy networks. For the synthesis of the siloxane-containing epoxy network, Bisphenol A diglycidyl ether (DGEBA) has been cured with commercially available siloxane-containing amine hardener 1,3-bis(3-amino-propyl)-1,1,3,3-tetramethyl disiloxane (BAS) (Scheme 2)



Scheme 2 Mechanism for F^- -catalyzed siloxane exchange



Scheme 3 Epoxy network synthesized using DGEBA cured with BAS.

For the F^- -catalyzed epoxy networks, CsF was used as the catalyst because the large cation helps separate F^- from Cs^+ . Through experimentation with varying amounts of the catalyst, it was determined that entry 3 (as displayed in Table 1) had the highest level of effectiveness. Although there were not notable variances in T_g and gel fraction among the polymers, entry 3 exhibited the most encouraging stress-relaxation behavior. Subsequent research will be concentrated on this particular entry (as depicted in Figure 2).

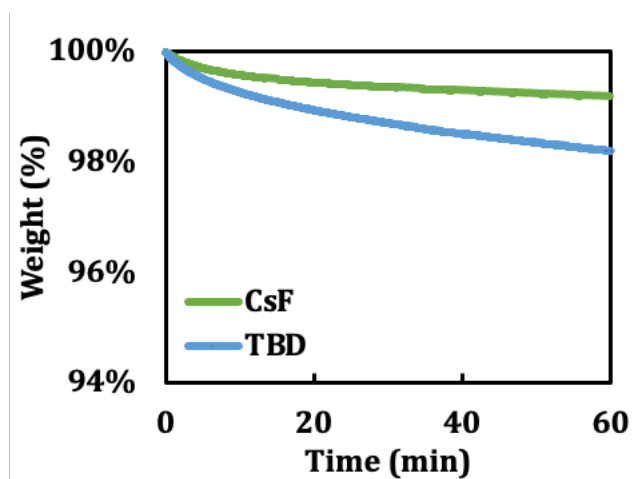
Additionally, this section will present a comparison between CsF-catalyzed and TBD-catalyzed epoxy networks. According to the scheme, the stoichiometric ratio between the DGEBA molecules and the BAS molecules is two. In the table, the catalyst mol% is based on the number of Si-O-Si functional groups in BAS. It is evident from the table that all the materials have T_g above 85 °C and gel fraction above 99%.

Table 1 Different amount of catalyst for the dynamic epoxy networks

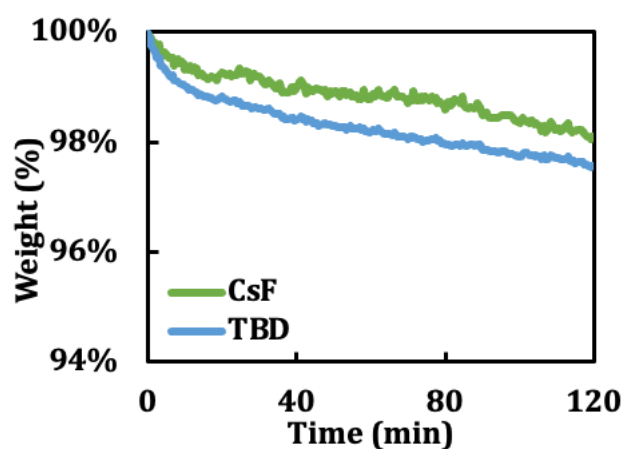
Epoxy Network	Amine (equiv)	Epoxy (equiv)	Catalysts	Catalyst (mol%)	T _g (°C)	Gel Fraction (%)
1	1	1.8	CsF	5	86.25	99.06
2	1	1.8	CsF	8	89.72	99.30
3	1	1.8	CsF	10	89.19	99.86
4	1	1.8	CsF	15	88.73	99.16
5	1	1.8	CsF	20	85.44	99.06
6	1	1.8	TBD	10	85.08	99.28

Next, the epoxy networks (Epoxy Network 3) were subjected to compression molding at temperatures between 160 °C and 200 °C after the material was cured. According to the isothermal TGA results, the F-catalyzed materials experienced a minimal weight loss of only 0.8%, while the TBD-catalyzed materials experienced a slightly higher weight loss of 1.8% after one hour at 200 °C with continuous airflow (Figure 1A). After two hours at the same temperature and flow rate, the F-catalyzed system lost 1.91% of its weight, while the TBD-catalyzed system lost 2.45% (Figure 1B). At 300 °C with constant air flow, the F-catalyzed materials showed a weight loss of 6.14%, while the TBD-catalyzed materials lost 5.50% of their weight after two hours (Figure 1C). When subjected to constant nitrogen flow at the same temperature and time, the F-catalyzed materials had a weight loss of 15.57%, while the TBD-catalyzed materials lost 13.66% (Figure 1D).

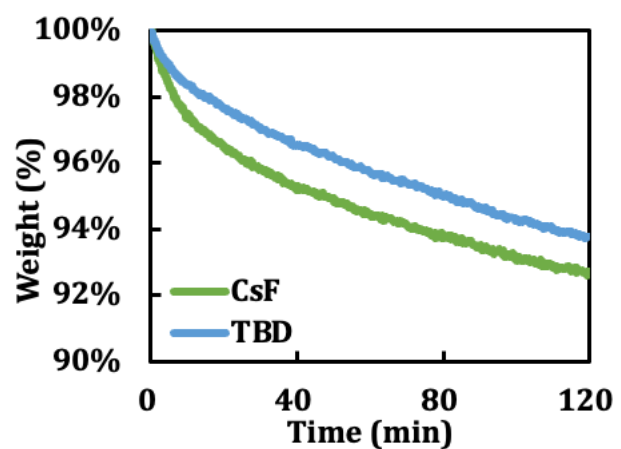
A)



B)



C)



D)

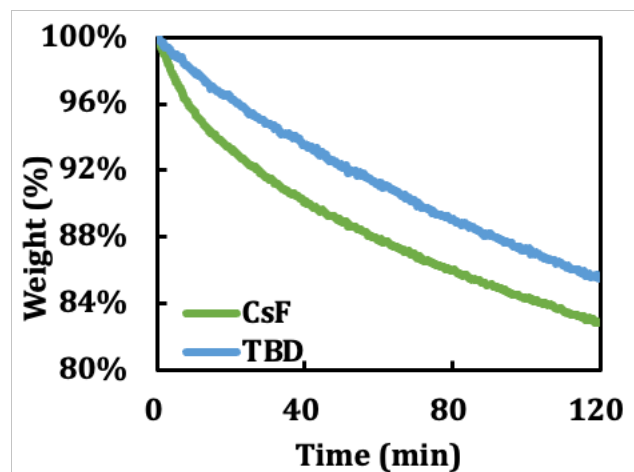


Figure 1. Thermogravimetric analyses of polymer with CsF and TBD. A) Isothermal TGA at 200 °C under air flow for 1 h. B) Isothermal TGA at 200 °C under air flow for 2 h. C) Isothermal TGA at 300 °C under air flow for 2 h. D) Isothermal TGA at 300 °C under nitrogen flow for 2 h.

Aided by different types of catalysts, the dynamic exchange behavior in each of the epoxy networks has been measured by rheology. Based on stress-relaxation measurements, it is evident that the material containing 10 mol% CsF exhibits a more rapid dynamic exchange when compared to other CsF concentrations (Figure 2A, B). Furthermore, the material with 10 mol% CsF has a faster relaxation rate than the material with 10 mol% TBD (Figure 2C, D).

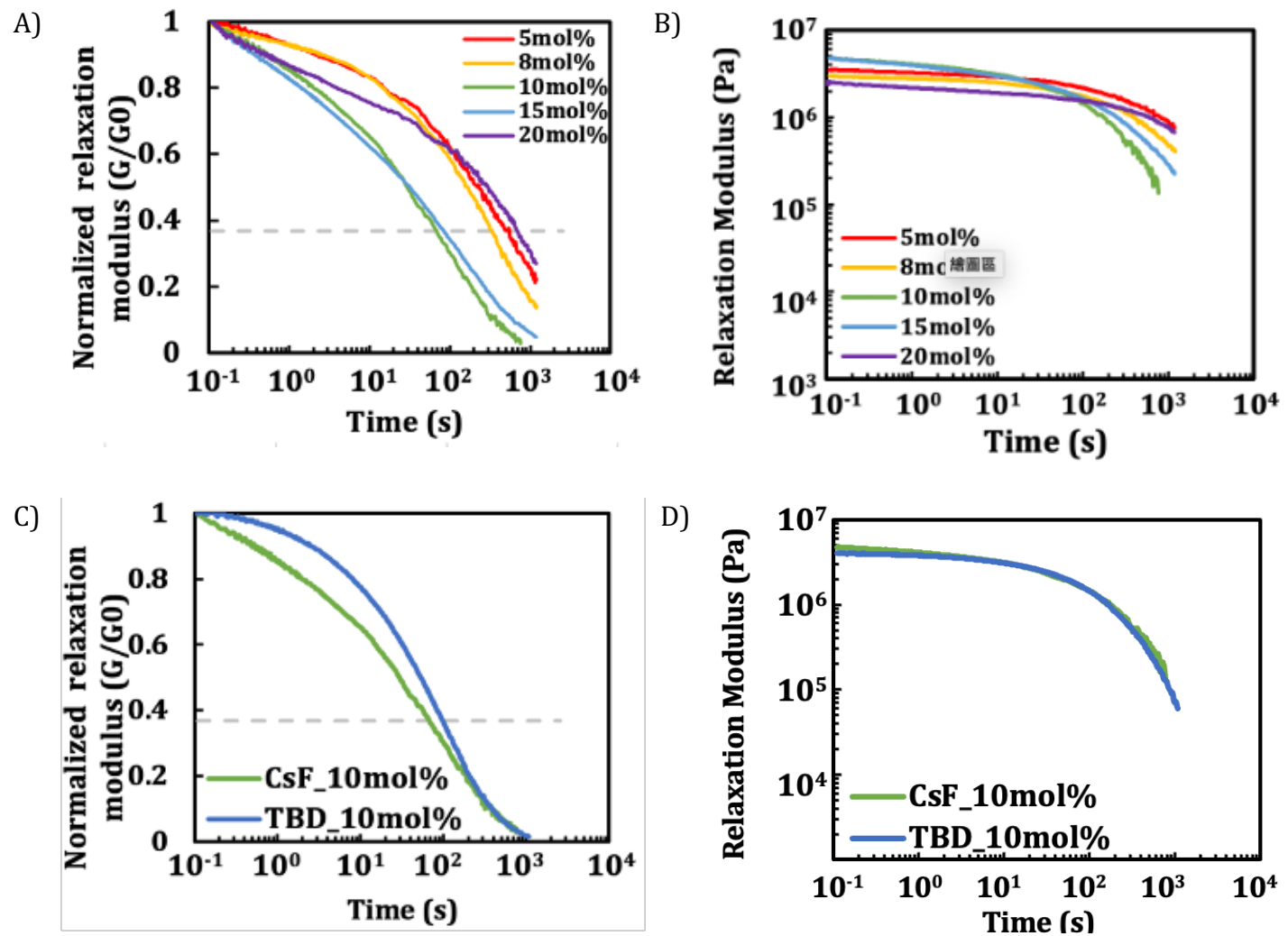


Figure 2. Stress-relaxation analyses. A) Normalized stress-relaxation plot of the materials with different amounts of CsF. B) Non-normalized stress-relaxation plot of the materials with different amounts of CsF. C) Normalized stress-relaxation plot of the materials with

different catalysts. D) Non-normalized stress-relaxation plot of the materials with different catalysts.

By examining the properties of materials catalyzed with CsF, we have discovered that their stress relaxation conforms to an Arrhenius temperature dependence. By varying the temperature between 160°C to 200°C and finding the characteristic relaxation time (when the modulus has reached 1/e of its original value), an Arrhenius plot can be created (Figure 3A), from which the activation energy of the dynamic exchange epoxy network catalyzed by CsF is calculated to be 40.6 kJ/mol (Figure 3B). This value is significantly lower than that for the same materials catalyzed by TBD, which have an activation energy of 87 kJ/mol³. The activation energy I obtained here was the same as previously reported fluoride exchange by Tretbar et al³⁵.

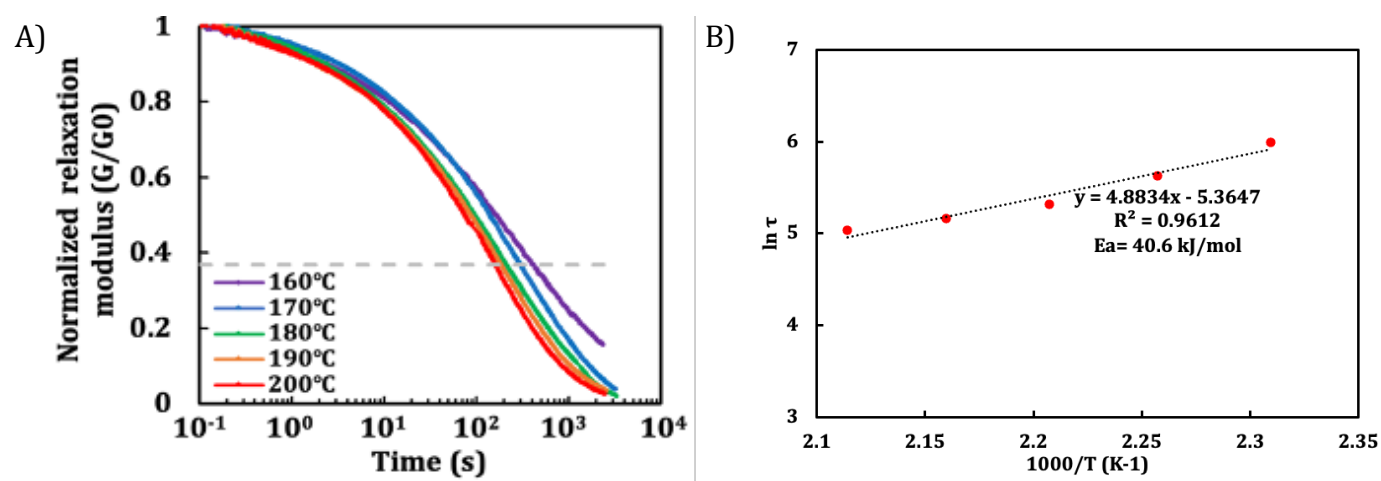


Figure 3. A) Normalized stress-relaxation plot of the materials with 10 mol% CsF in different temperatures. B) Arrhenius plot of material with 10 mol% CsF.

In order to understand material flow and viscosity during processing, frequency sweep experiments were conducted at different temperatures, from 170 °C to 200 °C

(Figure 4A). A constant shear storage modulus G' has been observed at high frequencies. The complex viscosity result follows the trend that the higher the temperature, the lower the complex viscosity (Figure 4B). Because of the dynamic exchange of siloxane cross-links, shear-thinning behavior has been observed. According to Figure 4A, the storage modulus stabilized, which indicates the CsF-catalyzed mechanism is responsible for the exchange process, and the total number of bonds remains constant. This indicated that in the temperature range, siloxane material can be easily reprocessed as its complex viscosity under high shear is suitably low.

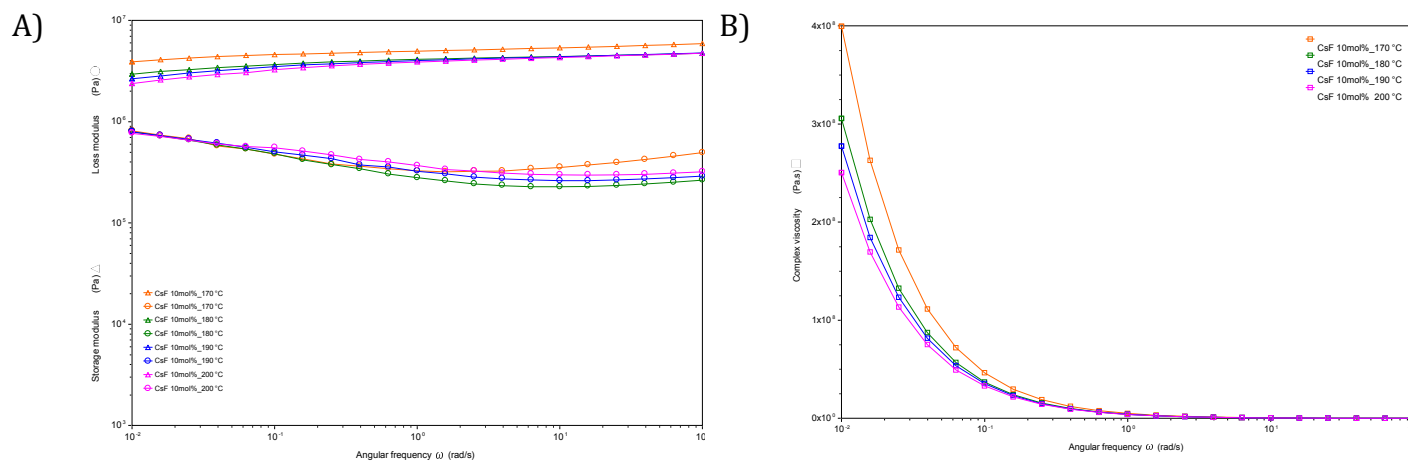
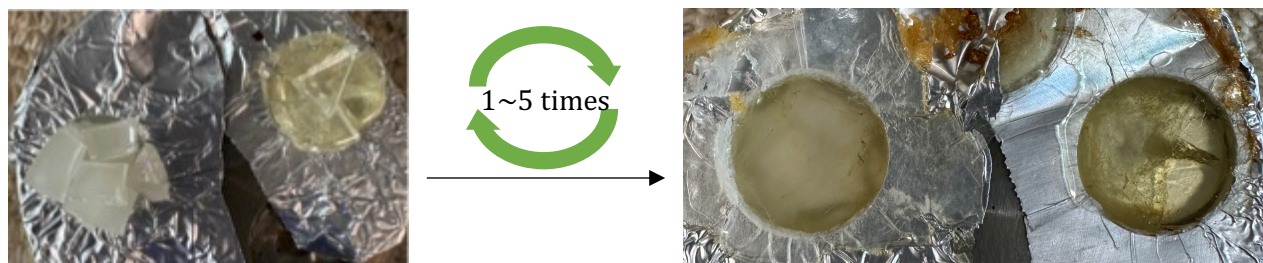


Figure 4. A) Frequency sweep experiments of materials with 10 mol% CsF at different temperatures. B) Complex viscosity of materials with 10 mol% CsF at different temperatures.

In order to determine if the CsF epoxy network could be recycled while retaining the ability of CsF to serve as a catalyst, the material was broken into smaller pieces and then compression-molded at a temperature of 200°C for five cycles (Scheme 4). The materials will be labeled as RX where X represents the number of reprocessing; for example, materials reprocessed once will be labeled as R1. Recent works from Debsharma et al.³

have demonstrated the reprocessing of the polymer using TBD catalyst for up to three cycles. The aim of this study is to further extend the cycle to five. This work builds upon the previous research and aims to investigate the effectiveness of catalysts in reprocessing the polymer in a more sustainable and efficient manner.



Scheme 4 Mechanical reprocessing of siloxane-containing dynamic epoxy networks at 200 °C through compression molding.

It has been observed that the color of the materials tends to become darker during the recycling process, regardless of the presence of CsF or TBD. Figure 5 illustrates that the samples containing 10 mol% CsF exhibit less cracking compared to those containing 10 mol% TBD, this means the dynamic exchange rate of CsF-catalyzed epoxy networks is faster.

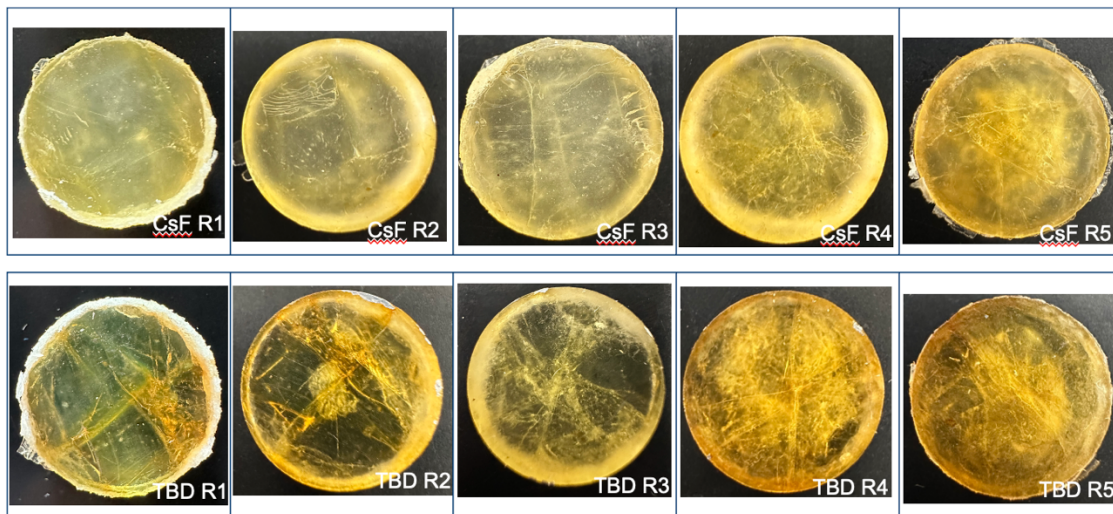
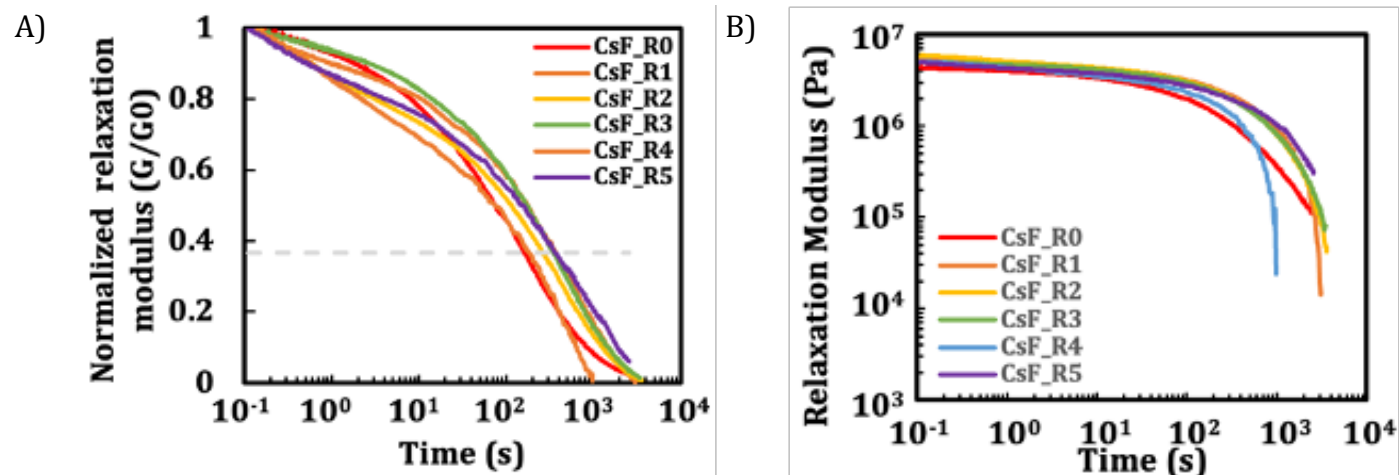


Figure 5 Pictures of samples after reprocessing.

Results from stress relaxation measurements indicate that even after undergoing reprocessing five times, the relaxation rate of the samples remains comparable to that of the original material (Figure 6). This finding suggests that the vitrimer properties are maintained even after multiple processing cycles, highlighting its potential for use in reshaping applications.



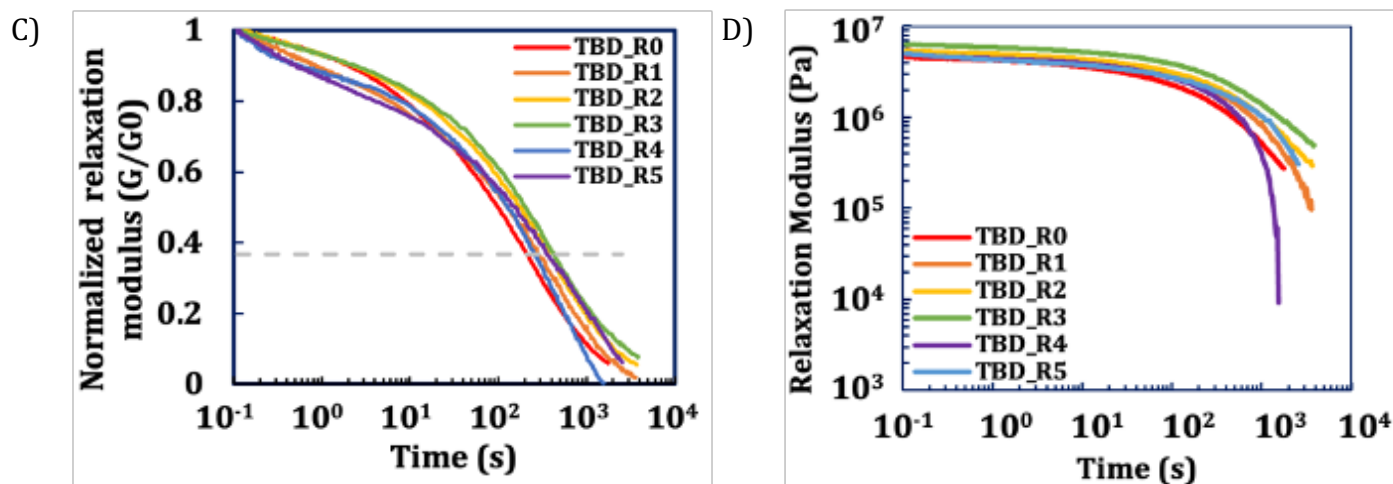


Figure 6 A) Normalized stress-relaxation plot of materials containing CsF after reprocessing. B) Non-normalized stress-relaxation plot of materials containing CsF after reprocessing. C) Normalized stress-relaxation plot of materials containing TBD after reprocessing. D) Non-normalized stress-relaxation plot of materials containing CsF after reprocessing.

Throughout the reprocessing, the gel fraction of the materials remained consistently high, with a percentage of over 98%. This is indicative of a robust and highly cross-linked network that remains stable and structurally sound throughout the multiple cycles. These findings suggest that the material is capable of retaining its integrity and strength even after undergoing several rounds of reprocessing, making it a reliable and durable option for a range of applications.

Table 2 Gel fraction of materials after reprocessing.

Name	Gel Fraction	Name	Gel Fraction
CsF 10mol%_R0	99.16%	TBD 10mol%_R0	99.00%
CsF 10mol%_R1	99.71%	TBD 10mol%_R1	99.03%

CsF 10mol%_R2	98.92%	TBD 10mol%_R2	99.33%
CsF 10mol%_R3	99.65%	TBD 10mol%_R3	98.76%
CsF 10mol%_R4	99.86%	TBD 10mol%_R4	99.19%
CsF 10mol%_R5	99.86%	TBD 10mol%_R5	99.05%

2.3 Conclusions and Future Work

The dynamic exchanging behavior of siloxane has been studied using CsF catalysts in this research. The synthesis of siloxane-containing epoxy vitrimers has been made possible by the discovery of a CsF-catalyzed pathway for siloxane exchange in epoxy networks. The CsF-catalyzed materials have been proven to be mechanically reprocessable at least five times while maintaining the same stress relaxation rate as the initial use. The isothermal TGA results demonstrate that the CsF-catalyzed dynamic materials will only lose less than 1% of their weight at the operation temperature. The gel fraction of the materials indicated that they remained highly cross-linked even after five reprocessing cycles.

2.4 Experimental

Chemicals. Bisphenol A diglycidyl ether (DER332, epoxy equivalent weight 176 g/mol), 1,5,7-Triazabicyclo[4.4.0]dec-5-ene (98%), was purchased from Sigma Aldrich. 1,3-Bis(aminopropyl)tetramethyldisiloxane (94%) was purchased from Alfa Aesar. Cesium fluoride (99.9%) was purchased from Thermo Fisher Scientific.

Synthesis of Epoxy Networks. CsF dissolves in methanol and mixes thoroughly using a vortexer at 2500 rpm for 1 min. Then, at a temperature of 45 °C, melt DGEBA until it becomes liquid and mix it with BAS using a vortexer at 2500 rpm for 1 min. Then mix the CsF-methanol solution with the DGEBA-BAS mixture. To properly complete the process, it is imperative to remove the methanol by utilizing a rotary evaporator at 50 °C for a full 10 minutes. Following this, pour the methanol-free mixture into the mold and allow it to cure for 1.5 hours in a vacuum oven at 70 °C and for 2.5 hours in a vacuum oven at 150 °C.

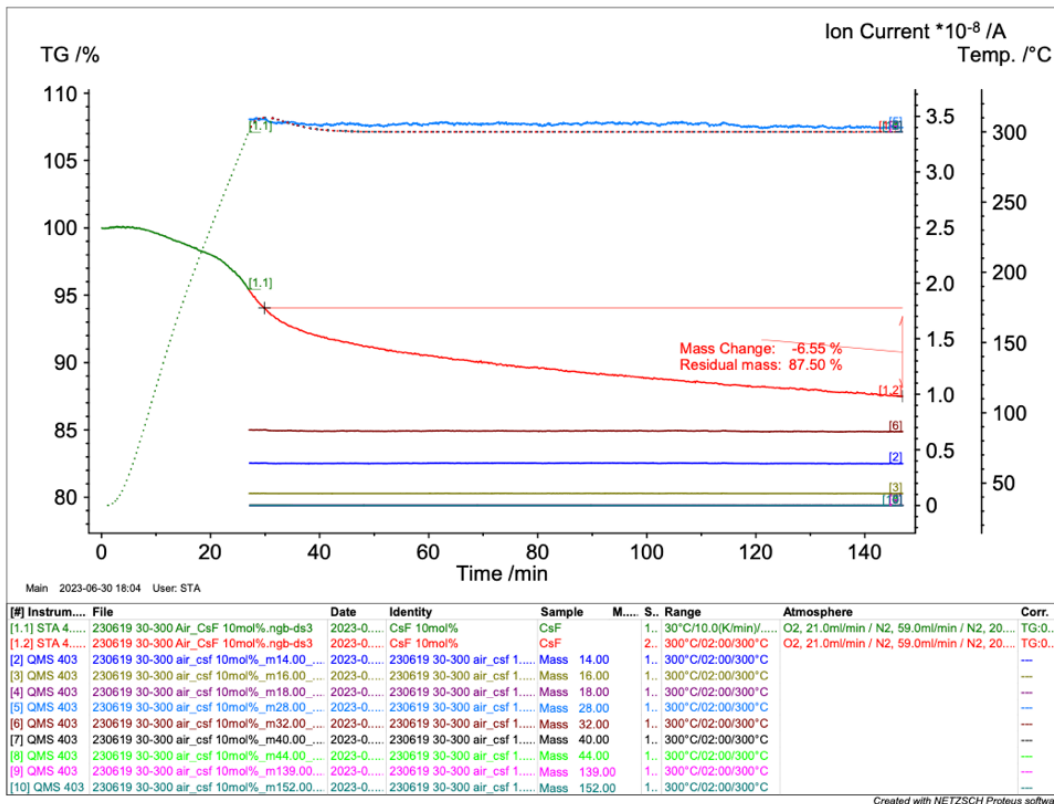
Instrument. Thermogravimetric analyses (TGA) were performed on the NETZSCH STA 449 F3 Jupiter® simultaneous thermal analyzer (STA) and TA Instruments Thermogravimetric Analyzer (TGA) Q500. The isothermal thermogravimetric measurements were performed under both air and nitrogen flow at 200 °C and 300 °C for 60 min and 120 min with a heating rate of 10 °C/min. Differential scanning calorimetry (DSC) measurements were performed on Discovery series DSC 2500 from TA Instruments under a nitrogen atmosphere with a heating rate of 10 °C/min and a cooling rate of 10 °C/min, and a temperature range from -50 °C to 200 °C. Stress relaxation measurements were performed on the Discovery series Hybrid Rheometer (HR-2) from TA Instruments with 12 mm plate shape geometry and used a normal force of 10 N with a frequency of 1 Hz and a strain of 0.25% (determined by amplitude sweep experiments).

Material Reprocessing. To reprocess the materials, first, use a cutter to break the sample into small pieces. Then, place them into a metal mold with five 14mm diameter and 3mm depth cylinders for compression molding. In order to close the mold, a metal plate will be utilized, followed by placing it in a hot press set at a temperature of 200 °C, with a

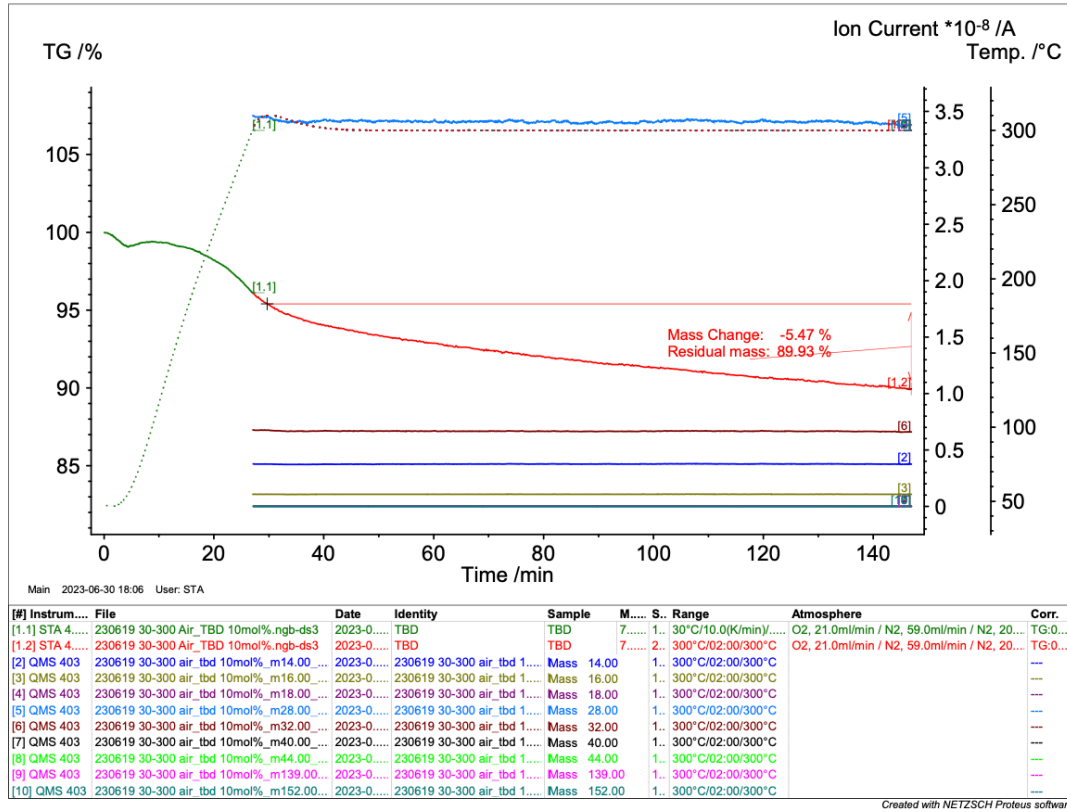
weight of 1 ton for 5 minutes to preheat. After preheating, the weight will be raised to 7 tons and the processing temperature will be sustained at 200 °C for 30 minutes. Following the compression molding process, it is necessary to allow for the cooling of the mold before proceeding to the removal of samples.

Representative isothermal TGA with mass spectroscopy analysis

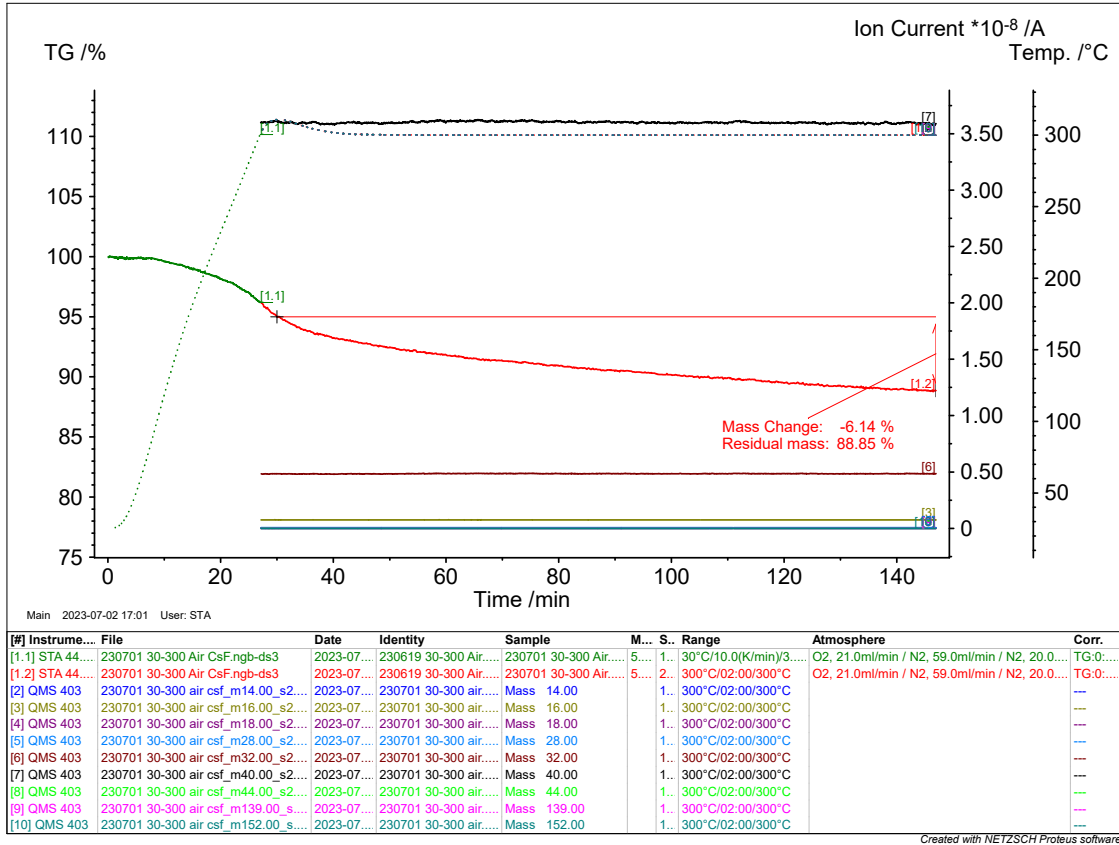
Isothermal TGA of material contains 10 mol% CsF at 200 °C under airflow for 2h.



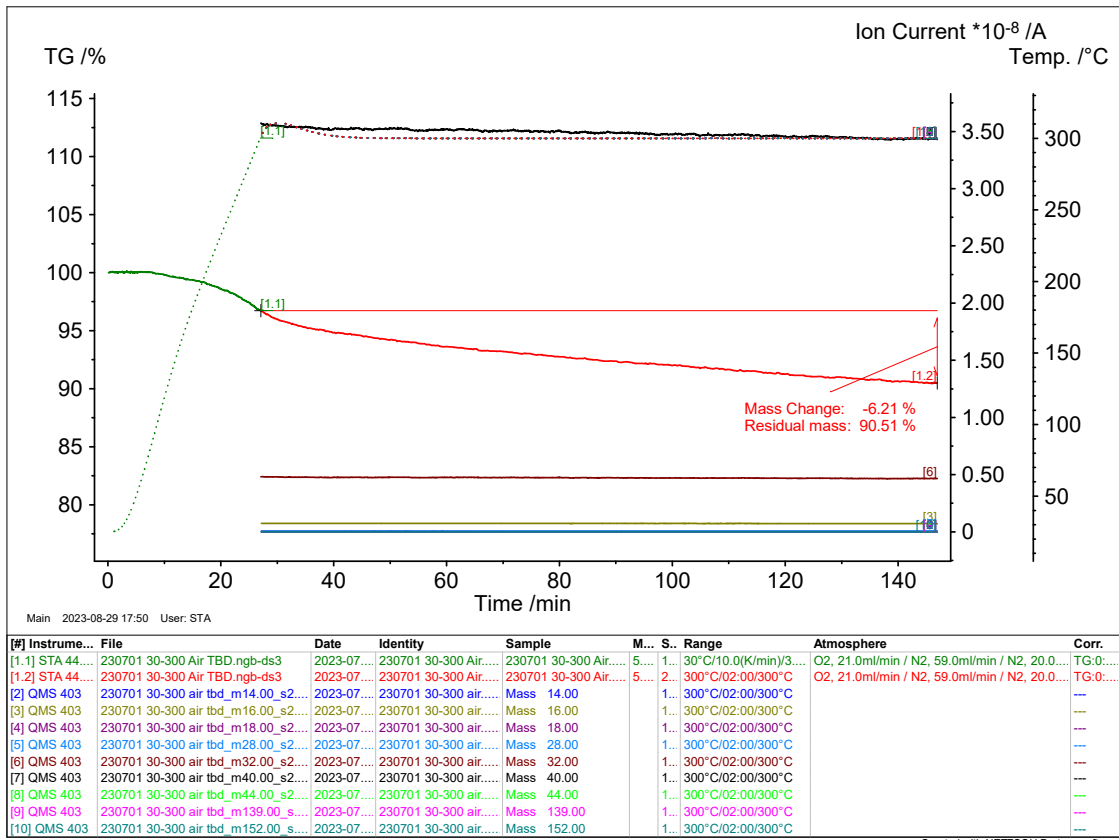
Isothermal TGA of material contains 10 mol% TBD at 200 °C under airflow for 2h.



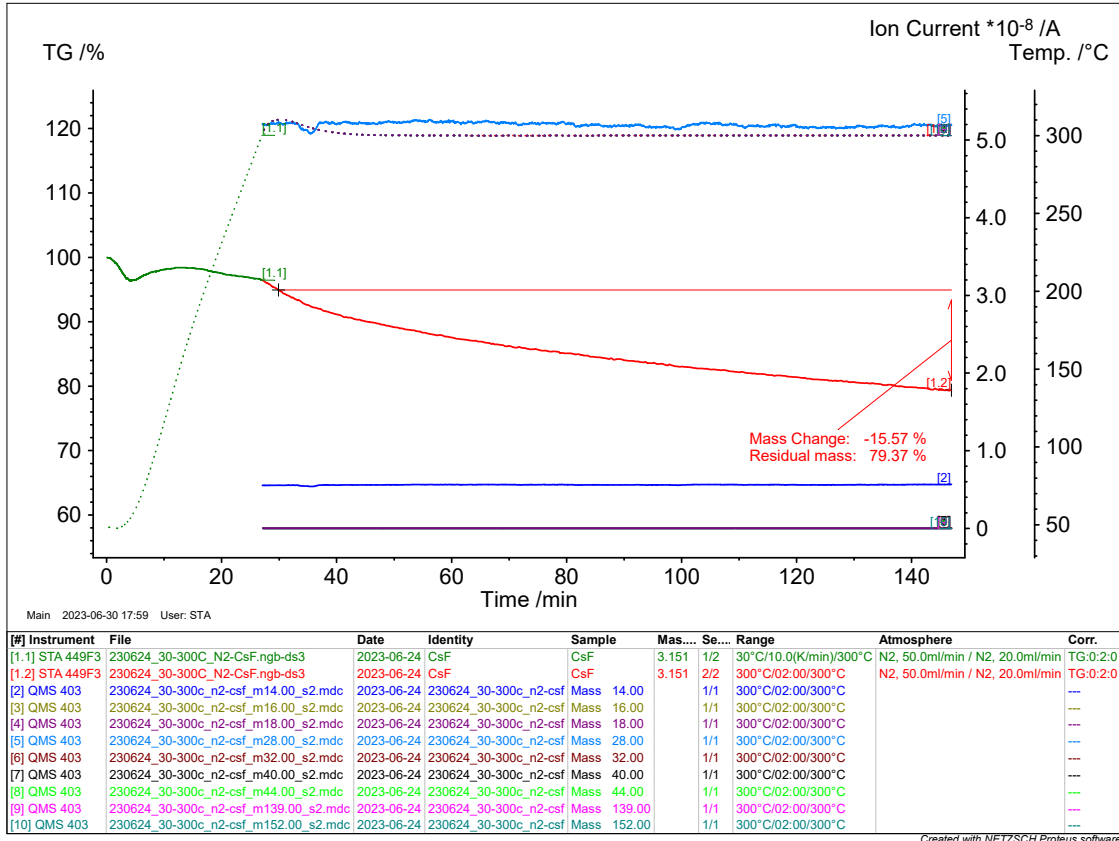
Isothermal TGA of material contains 10 mol% CsF at 300 °C under airflow for 2h.



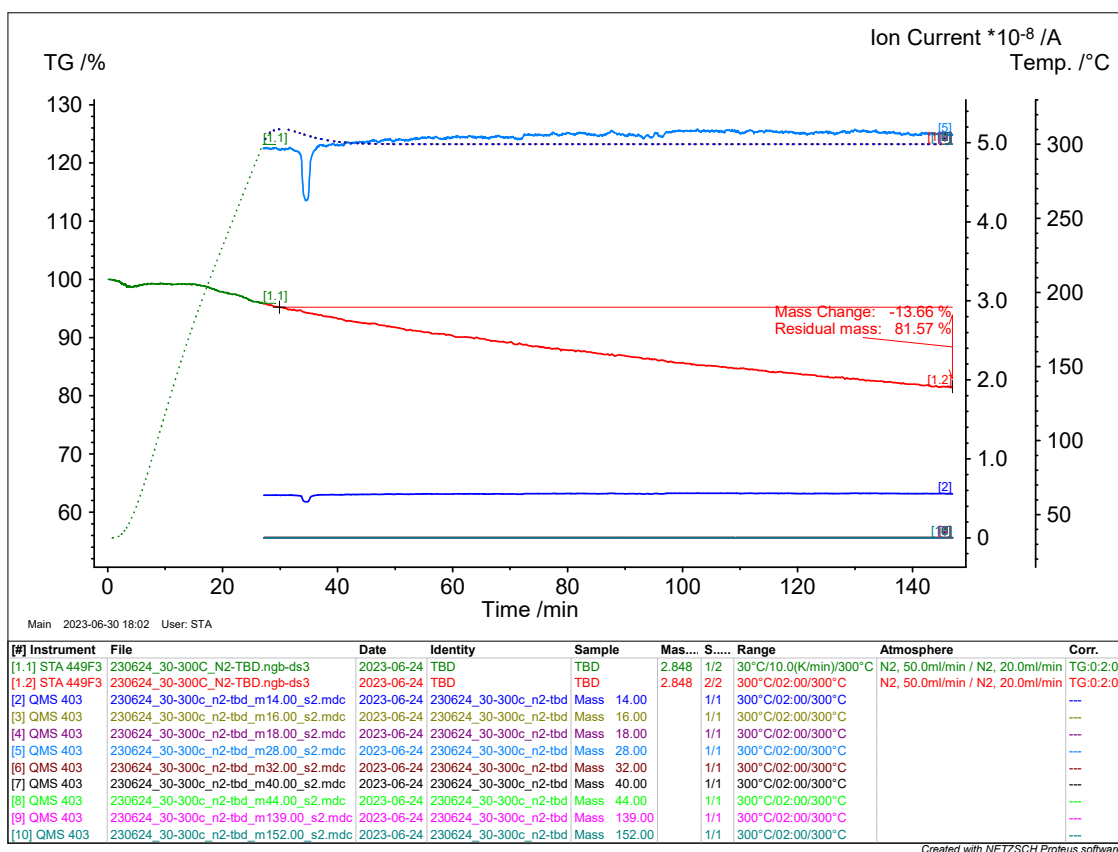
Isothermal TGA of material contains 10 mol% TBD at 300 °C under airflow for 2h.



Isothermal TGA of material contains 10 mol% CsF at 300 °C under nitrogen flow for 2h.



Isothermal TGA of material contains 10 mol% TBD at 300 °C under nitrogen flow for 2h.



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