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Analysis of the Mechanical Properties of DGEBF/4,4'-DDS Thermoset Systems as a Function of Cure Rate

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The University of Southern Mississippi

Analysis of the Mechanical Properties of DGEBF/4,4'-DDS Thermoset Systems as a
Function of Cure Rate

by

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Submitted to the Honors College of
The University of Southern Mississippi
in Partial Fulfillment
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Bachelors of Science
in the Department of Polymer Science

May 2015

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Abstract

The relationship between macroscopic mechanical and thermal properties and ramp rate during cure of epoxy-amine systems consisting of the epoxide resin diglycidyl ether of bisphenol F (DGEBF, provided Hexion specialty chemicals) and 4,4-diaminodiphenyl sulfone (4,4-DDS, provided by Atul Sulpho) were probed using Dynamic Mechanical Analysis (DMA), Positron Annihilation Lifetime Spectroscopy (PALS), and compression testing. These systems were cured in a programmable oven; the samples were heated from 35°C to 180°C at ramp rates of 0.5, 1.0, 1.5, 2.0, 2.5, 5.0, 10, and 15°C/min.

Even as the ramp rates during the cure of these materials was changed, there was very little in properties such as crosslink density, glass transition temperature (T_g), free hole volume, or modulus in the samples.

Keywords: Epoxy-amine, thermosets, network formation, thermoset matrix

Dedication

To my parents, Nancy and Byron, and my sisters, Courtney and Morgan, for their
unwavering love and support.

Acknowledgements

I would like to thank my adviser, Dr. Wiggins, for his support and friendly encouragement. This research would not have been possible if he hadn't been there to guide me. Thank you for everything.

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List of Abbreviations

- DGEBF – Diglycidyl ether of bisphenol F
- DGEBA – Diglycidyl ether of bisphenol A
- TGAP – triglycidyl ether of para-amino phenol
- TGDDM – tetraglycidyl diamino diphenyl methane
- 4,4-DDS – 4,4-diamino diphenyl sulfone
- T_g – Glass transition temperature
- IR – Infrared
- DMA – Dynamic mechanical analysis
- PALS – Positron annihilation lifetime spectroscopy

Chapter 1: Introduction

An issue with modern day aviation is the weight of the aircraft. As fuel prices continue to increase, the importance of efficiency of weight continues to grow. New precautions are always being taken to cut down on costs or increase net monetary gain for the airline company; often these ‘precautions’ lead to an increase ticket fares in commercial planes. Saving weight—even just a few pounds—can mean saving large sums of money for an airline, and an overall decrease in both production and ticket prices. In fact, reducing the weight of a few different plane models by only 1% could reduce the cost of fuel enough for a company to annually save anywhere from \$45,000 to \$5.6 million depending on the size of the aircraft in question.¹

An obvious place to start with the weight of an aircraft is with the heaviest component of many planes: the metal alloys used to build them. Metals are so dominant in the field of aviation is the excellent mechanical and thermal properties they offer.

Scientists have turned to polymers, especially polymer composites, to build these aircrafts, but this raises a number of issues. A composite is a material consisting of a polymer matrix system and an added fiber, or a material often on the nanometer scale that exists in the matrix to reinforce the mechanical properties.³ Not only does the polymer composite need to withstand the stresses experienced in flight, but the material also needs to withstand the effects of the environment such as constant exposure to ultraviolet radiation and moisture in the atmosphere. The chosen polymeric material would need to exhibit the best in chemical and mechanical properties in order to replace the metal alloys that have dominated the field of aviation for so long.

The bulk properties of the resulting composite material do not stem from the matrix or fiber alone, but instead it has been suggested that the mechanical properties are dictated by the interphase region between the fiber and matrix—or the area in which the bulk fiber is in direct contact with the bulk matrix and interactions occur.¹⁷ The matrix and its structure plays a large part in how this interphase interaction occurs, so understanding the formation of the resulting network will be important to understand more about the interaction between the fiber and polymer matrix.

1.1: Thermosets

In the field of plastics processing, polymer materials are typically split into two categories: thermoplastics and thermosets. A thermoplastic is a material that, once synthesized and processed, can be melted down, reformed, cooled, and reused almost an indefinite number of times.⁴ The individual polymer chains are held together only by weak, intermolecular Van der Waal's forces; upon heating, these weak forces between chains are broken but are easily reformed.² On the other hand, thermosetting polymers form crosslinks and cannot be melted after being processed. Further heating will cause the material to soften and eventually degrade.³ Crosslinking is a process by which strong covalent bonds are formed between polymer chains. For crosslinks to form, functionality greater than two is required on either the resin and/or curing agent. In these thermosetting systems, the 'resin' is the matrix component that offers the majority of mechanical and thermal properties in the resulting matrix; the curing agent, on the other hand, is a means by which to create a favorable environment in which the resin can crosslink by adding a highly reactive, multi-functional chemical group.

When a resin is first reacted with a curing agent, the monomer units begin to react with one another and slowly begin to build themselves into oligomer units. These oligomer units will continue to build up to larger molecular weights. However, when a certain molecular weight and degree of polymerization—or the amount of monomer repeat units present on an active chain—is achieved, the present oligomer chains begin to react with one another. This point is either known as the critical molecular weight, M_c , or gel point of the polymerization, p_{gel} . At this point, enough of the resin and curing agent molecules have reacted to create an environment in which reactive chain sites meet. The viscosity of the system increases, and curing occurs. Curing can take place at room temperature, but often times a high temperature cure cycle is used to minimize the amount of chains that continue to cure after the cure cycle has finished.

Thermosets typically move through three stages of a reaction termed the A-, B-, and C-stage; each stage corresponds to a point in the reaction that relates the extent of the reaction or conversion of the reaction (p) to the p_{gel} . In the A-stage, the $p < p_{gel}$. At this point in the reaction, the solution is both fusible and soluble. In the B-stage, p is approaching or close to p_{gel} , so the viscosity of the system increases and it becomes insoluble. Finally, when the solution enters the C-stage, p has surpassed p_{gel} by a significant margin and the product has cured, meaning it is both insoluble and infusible.⁴

Thermosets have been valued industrially for their good mechanical properties. Since thermosets do not melt, they tend to operate better at higher temperatures than thermoplastics. However, there is still an upper limit at which thermosetting resins can be used since they will soften and lose some of their desired properties. Thermosets offer a high modulus and good strength properties, making them highly desired when strenuous

work is being done. Thermosets have a higher specific modulus than metals—meaning thermosets have a better resistance to deformation as a ratio of the material's density. Being lighter makes thermosets highly sought after in areas where a material's weight is an issue.

1.2: Epoxy-Amine Systems

Epoxy resins are the most common type of modern resin. Epoxy resins get their name from the epoxide functional group that is found on these types of systems.

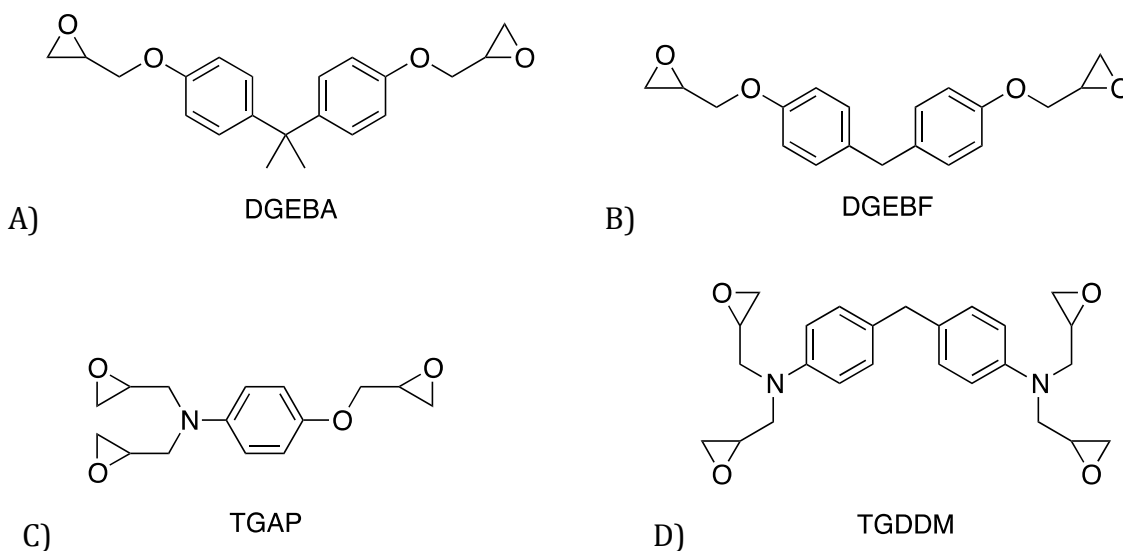


Figure 1: Common epoxy resins, DGEBA (A), DGEBF (B), TGAP(C), TGDDM(D)

The popularity of epoxy-based systems from their heat resistance, corrosion resistance, low shrinkage during cure, and low coefficients of thermal expansion.³ Epoxy-based systems are also advantageous because they require no solvent and give off no by-products during their reaction. They have found use as strong adhesives, corrosion-resistant coatings, and are beginning to find a niche in aerospace applications as a lightweight-alternative to metal alloys.⁵

Epoxide resins were first mentioned in some scattered patents throughout the 1920's and early 1930's. A scientist by the name of Moss was the first to acknowledge that epoxide compounds carried resin characteristics typical in thermosetting materials in his patent application submitted in December of 1937.⁵ In 1938, a patent application was submitted by the Swiss chemist Castan describing the synthesis of diglycidyl ethers and esters through the use of diphenylolpropane (DPP) and epichlorohydrin. He polymerized these resins with acid anhydrides, leading to what can be considered some of the first epoxy-based thermosets. A Swiss company by the name of CIBA A.G. acquired Castan's patent and began to produce epoxy resins for commercial uses to bind light alloys or as electrical insulators.⁵ At the same time, an American paint company—Deyoe and Reynolds—began to produce and sell epoxy resins. They were the first to market a line of 'Epon' resins, which are still considered to be one of the most important families of epoxy resins still in production.⁵

In epoxy resins, the epoxide rings experience a large amount of ring strain and will react freely in a ring opening, step growth reaction mechanism. To encourage and accelerate the growth of these resins, curing agents are commonly used to ensure that a large number of crosslinks form. Amines are a common form of curative due to their high reactivity and high functionality per amine.

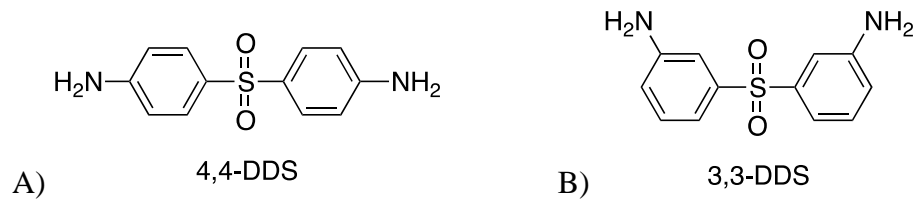


Figure 2: Structure of amine curatives 4,4-diaminodiphenyl sulfone (A) and 3,3-diaminodiphenyl sulfone (B)

The reaction begins with the amine ring-opening the oxirane, producing a hydroxypropyl ether which contains a hydroxyl group and a secondary amine. This reaction will continue in a mostly linear fashion until the M_c is reached, wherein the secondary amines will begin to react with oxirane groups, reacting all epoxide functional groups and producing tertiary amines. At high enough temperatures, the hydroxyl groups from the opened rings can ring-open other oxirane groups in an etherification process.⁶

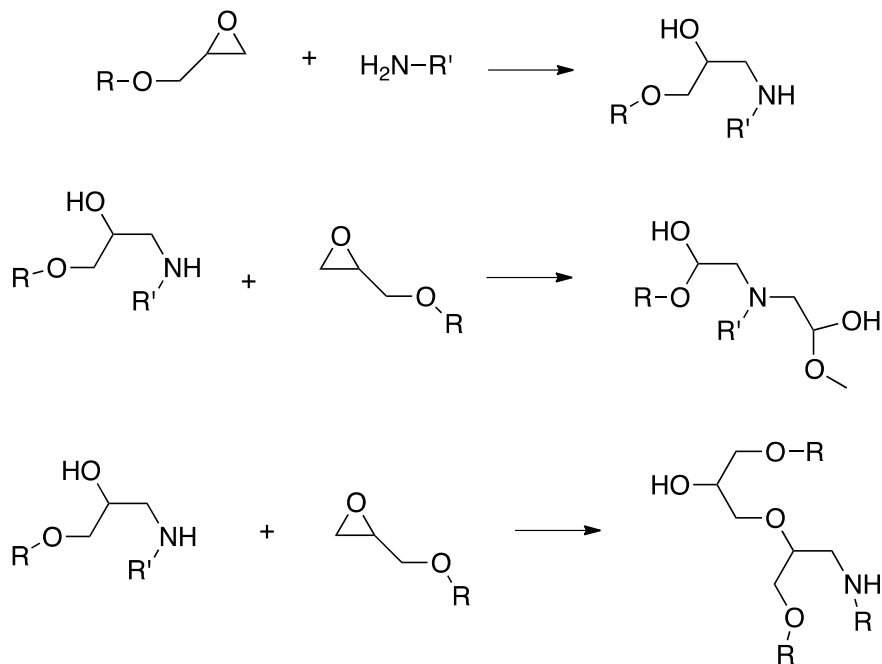


Figure 3: Crosslinking mechanism for epoxy-amine systems

Most commonly, the resin diglycidyl ether of bisphenol A (DGEBA) is used commercially and has likewise been the focus of many studies pertaining to the resin's chemical and mechanical properties. Sahagun *et al.* inspected the network growth of a low molecular weight DGEBA oligomer reacted with the curing agent 3,3-diaminodiphenyl sulfone (3,3-DDS) and found that the majority of network growth of the crosslinked matrix begins after the gelation point has been reached in a process known as active network growth.⁷ This stage ends upon the onset vitrification, or the point where the glass transition temperature (T_g) of the material approaches the reaction temperature; vitrification is a thermally reversible process. It was found that once the post-vitrification stage was reached, diffusion of reactants through the crosslinked system became difficult due to the crosslink density preventing movement through the system; however, if the system were to be heated above its maximum T_g temperature (often called T_g infinity), then diffusion can continue throughout the system.¹⁹ The amine was found to add first in a linear fashion during the pre-gelation stage, becoming a secondary amine, before being converted into a tertiary amine during the stage of active network growth, where the majority of crosslinks are formed.

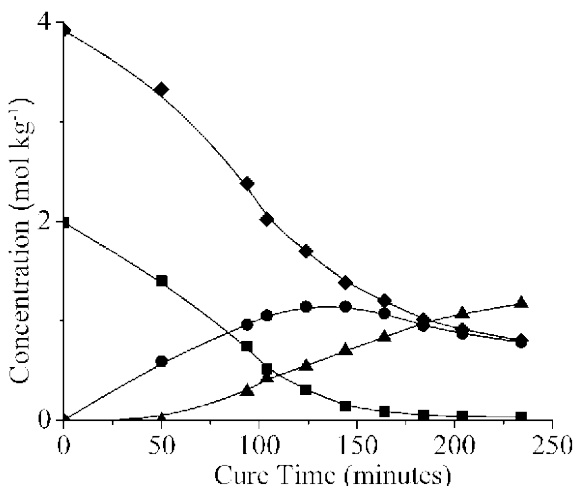


Figure 4: Infrared Spectroscopy (IR Spectroscopy) data for epoxy-amine network growth shown tracking the concentration of epoxide (♦), primary amine (■), secondary amine (•), and tertiary amine (▲) as a function of cure time.

Other extensive studies on the mechanical properties of DGEBA and its network formation with a wide range of amines and other curing agents have also been performed.⁸⁻⁹ DGEBA has been characterized as a high performance thermosetting resin system with a large range of applications and widespread use in industry.

DGEBF, like DGEBA, is a di-functional epoxy resin often purchased as a low molecular weight oligomer since its monomer form has a tendency to crystallize at room temperature.¹⁰ Since it lacks the methyl groups of DGEBA (see Figures 1a and 1b), DGEBF tends to have more chain rotation about that. Because of its structure, DGEBF has a lower stiffness and T_g than DGEBA. Mijovic *et al.* showed that DGEBF and DGEBA react with the amine diaminodiphenylmethane at a similar rate, with DGEBF having a higher conversion early due to the lack of an isopropyl group in the center to restrict chain movement and rotation in the system.¹¹

1.3: Matrix Characterization

There are many methods commonly used to analyze the mechanical properties of thermoset polymer systems. One of the most popular methods is dynamic mechanical analysis (DMA). The most common form of DMA involves placing a rectangular sample of known length, width, and thickness into a DMA instrument and applying a sinusoidal stress to the sample over a particular temperature or frequency range.¹² The data most commonly gathered from this set of experiments is storage modulus (E') and loss modulus (E''). E' represents the elastic component of the sample being tested and E'' represents the viscous—or imaginary—component of the modulus and is also known as the energy dissipation term. These both make up the complex modulus of the system, given by the relationship

$$E^* = E' + iE''$$

Where E^* is the complex modulus and i is $\sqrt{-1}$. Since the stress and strain are not in phase of one another, a phase angle is also acquired through the experiment that represents the time lag between these two phases. The relationship between this angle and the individual moduli is given by

$$\tan \delta = E''/E'$$

This $\tan \delta$ is a measure of the ratio of the energy dissipated by the system in relation to the maximum energy stored by the system during one stress cycle. Since the $\tan \delta$ corresponds to viscous component over the elastic component, it can also be used to find the onset of viscous behavior in a material, which corresponds to the material's T_g . However, the T_g is also commonly extrapolated from the inflection point of the storage modulus as loss occurs.

Positron Annihilation Lifetime Spectroscopy (PALS) is a popular method for determining the volume of the voids (called “free volume”) present in materials; it relies on the use of positrons, which have similar properties to electrons but an opposing positive charge. While the primary application of PALS is its ability to give average free hole size, it can also indicate a material’s T_g , molecular dynamics, and blend miscibility.¹⁴ PALS typically uses ^{22}Na as a positron source. When positrons are injected into a sample, they can become trapped in vacancies within the sample.¹⁵ At some time δt —between the order of zero and a few hundred picoseconds—the positron will react with an electron, its antimatter, and annihilation will occur. Annihilation is a term describing the event in which a particle and its antiparticle interact and there is a change in the energy of both particles. In this case, a positron and electron interact and emit gamma rays.

During PALS, the source of the positrons is placed between two equivalent pieces of the sample being tested. During the run, a detector measure the time beginning with the emission of an initial gamma ray emitted at the same moment the positron is injected into the sample and stopping when a second gamma ray—that given off from the annihilation process—is detected. The instrument converts this time (δt) into an output pulse. These pulses have differing amplitudes and give the average electron density in the region in which the annihilation occurred.

Jackson *et al.* found that, for DGEBA/4,4-DDS and DGEBA/3,3-DDS networks, the average hole-size free volume increased as a function of the overall temperature of the curing system; as the system is cooled after reaction, the chain conformations—and therefore the voids associated with free volume—are locked into place.¹⁸ Solvent uptake

was shown to be primarily governed by the free volume hole size and the particle size of the organic solvent penetrant.¹

Chapter 2: Methods

This work is based off the use of thermosetting epoxy-amine polymer matrix materials. Diglycidyl ether of bisphenol F (DGEBF) was selected as model, difunctional epoxide resin. The amine curative 4,4-diaminodiphenyl sulfone was selected as a model amine curative that, when used as a crosslinking agent for the DGEBF resin, builds a tightly crosslinked thermoset system with properties that are analyzable using certain thermal and mechanical testing techniques. The preparation of these materials for use as neat resin systems will be discussed further in this section.

2.1: Resin

DGEBF or EPON 862 (Hexion Specialty Chemicals) was used as received. As provided, EPON 862 had an average molecular weight of 338 g/mol and an epoxide equivalent weight (EEW) of 169.

2.2: Amine Curative

4,4-DDS (Atul Sulfo, 97%, micronized) with a molecular weight of 248.3 and EHEW (extractable hydrogen equivalent weight) of 62.08 was dried in a vacuum oven for 24 hours at 50°C to remove any moisture content. The dried 4,4-DDS was stored in a desiccator to prevent the uptake of moisture before the material's use.

2.3: Epoxy-Amine Matrix Synthesis

These thermosetting systems were synthesized by adding a DGEBF into an Erlenmeyer flask with a vacuum fitting and magnetic stir bar. The resin was allowed to

stir at 65°C and a vacuum of approximately 10^{-3} torr was applied to the flask to remove air, moisture, or solvent impurities present in the resin. After degassing was complete, the vacuum was removed from the oven and the 4,4DDs was added to the epoxide at a 1:1 epoxide to active amine hydrogen ratio to give the highest theoretical conversion of the system. After the amine was added, the solution was stirred vigorously and a vacuum of 10^{-3} torr was reapplied to the flask. It was not uncommon to use acetone to wash excess amine from the transfer container or the sidewall of the flask. After the evolution of gas was no longer detectable to a large degree, the solution was heated to 125°C, the apparent solubilizing temperature of the amine in the epoxide resin. Upon amine dissolution, the resin was cast into various geometries to be cured. The cast resins were placed in a programmable oven set to heat from 35°C to 180°C at varying ramp rates; the samples were then held at 180°C for three hours to post cure. The ramp rates used in these cure profiles ranged from 0.5 to 15°C/min.

2.4: Dynamic Mechanical Analysis

Dynamic mechanical properties, including storage modulus (E') and T_g as extrapolated from the $\tan\delta$ (tan delta) peak were found using a Thermal Analysis (TA) Q800 DMA in tensile mode (strain amplitude 0.05%, frequency 1 Hz). The samples were ramped from 35°C to 250°C at 3°C/min.

2.5: Positron Annihilation Lifetime Spectroscopy

Samples for PALS analysis were cast as circular disks with diameters of approximately 1 cm and thickness of approximately 1-2 mm. Two identical sample discs were used to sandwich a 5 μCi ^{22}Na positron source that was then sealed between two

sheets of 13 μm thick klapton sheets. This was then wrapped in aluminum foil and placed into a vacuum canister.

2.6: Compression testing

Compression tests were conducted on machined cylinder samples with lengths between approximately between 18 and 21 mm and diameters of half their length (between 9 and 10.5 mm). Testing was performed using an MTS 810 hydraulic test frame with a cylindrical sub-press (Wyoming Test Fixtures). The tests were run in accordance with ASTM 695-02a. That displacement rate was 0.05 in/min and the tests were terminated at 30% strain.

Chapter 3: Results and Discussion

The ring-opening reaction of an epoxide ring with an amine is exothermic in nature. When these exothermic reactions occur, it is possible that the heat given off can further drive the reaction of the system. Thermoset polymers rely heavily on the cure profile because any network heterogeneity that forms during cure could lead to differences in mechanical and thermal properties.

3.1 Positron Annihilation Lifetime Spectroscopy (PALS)

PALS is a method by which the size of spherical voids within the matrix can be extrapolated. Free volume hole size dictates fluid uptake properties in a polymer network; larger free volume hole size means that moisture and organic solvents can move into the system by means of a less tortuous path.^{6,18}

Free volume hole size was extracted from the system using the equation

$$\tau_{o-ps} = 0.5 \left[1 - \frac{R}{R_0} + \frac{1}{2\pi} \sin \left(\frac{2\pi R}{R_0} \right) \right]$$

Where τ_{o-ps} are the ortho-positroniums, R is the radius of the cavity, and R_0 has a constant value of 1.66 Å. Using the radius of the cavity, the free volume hole size (v_h) can be found using the equation:

$$v_h = \frac{4}{3}\pi R^3$$

Figure 5 shows the free volume hole size data for the eight sample sets. The free volume holes all lie between on average of 55-60 Å³ in terms of volume. While there is a difference, there is no appreciable trend in hole size as a function of ramp rate during cure. Jackson *et al.* showed that for the uptake of organic solvents, the free volume hole size of thermosetting epoxy systems impacts how quickly—and how much—of an organic solvent that one of these networks can absorb. With a larger free volume hole size, more organic solvent can be absorbed and the rate at which it ingresses could increase if a less tortuous path is found.¹⁸ Since the free hole volume size is similar across these systems, it is likely that the formation of these voids occurred at similar rates and under similar conditions.

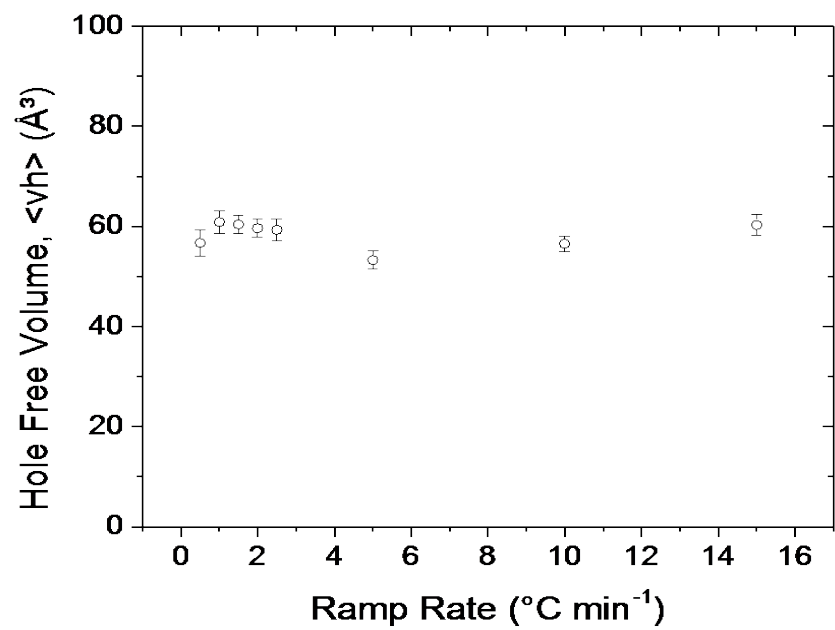


Figure 5: PALS data showing hole free volume vs ramp rate during cure

3.2 Dynamic Mechanical Analysis (DMA)

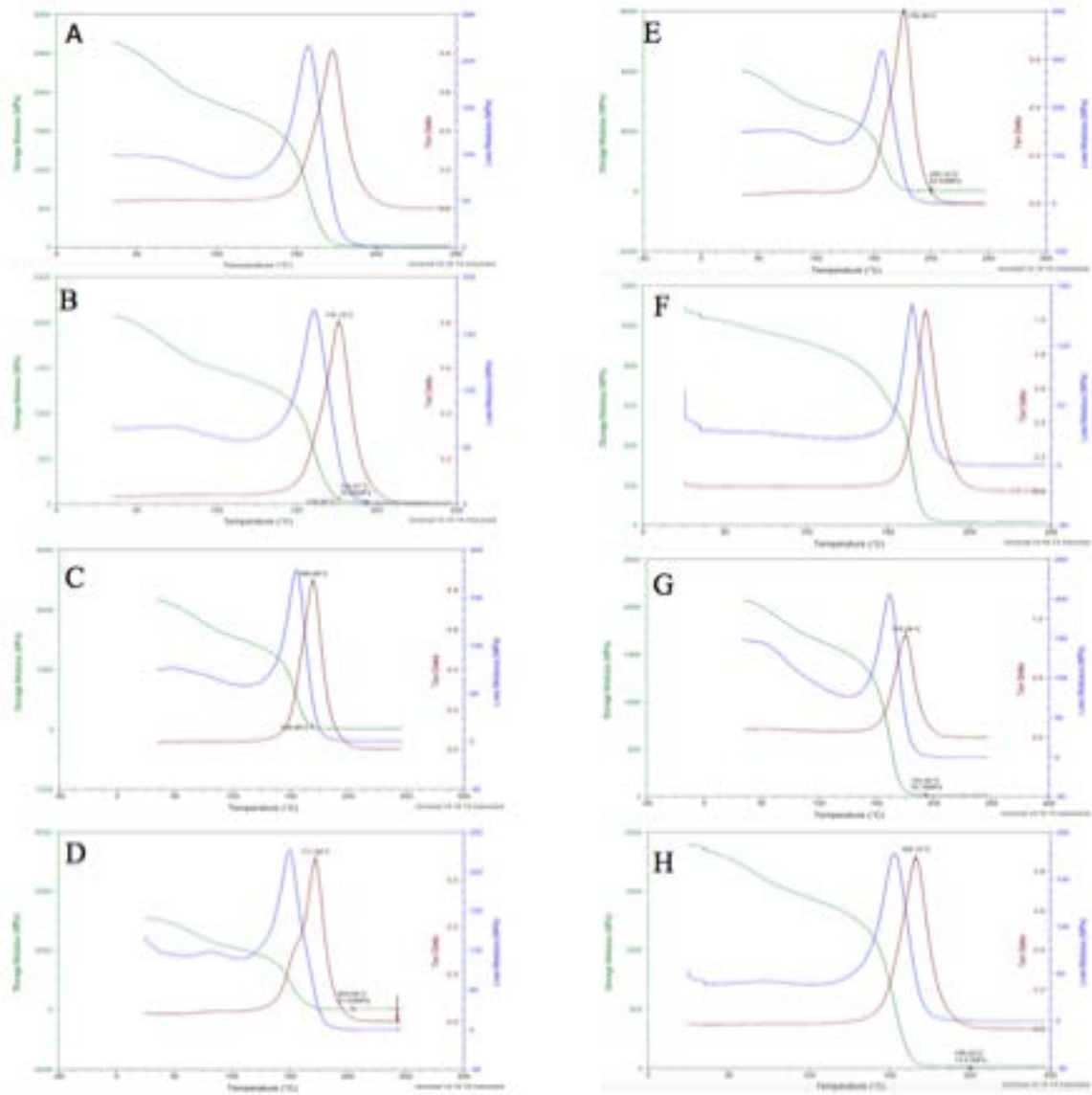


Figure 6: DMA data for 0.5 °C/min (A), 1.0 °C/min (B), 1.5 °C/min (C), 2.0 °C/min (D), 2.5 °C/min (E), 5.0 °C/min (F), 10.0 °C/min (G), and 15.0 °C/min (H) samples.

The glass transition temperature (T_g) of these systems were taken from the $\tan \delta$ peaks indicated by the red line in Figure 6. The T_g data for these systems, along with the crosslink density data (v_c)—which will be discussed later—can be found in Table 1.

Ramp Rate °C/min	T _g °C	v _c x 10 ³ mol/m ³
0.5	173	1.49
1.0	176	1.25
1.5	169	1.08
2.0	172	1.77
2.5	176	1.94
5	173	1.34
10	175	1.29
15.0	167	1.24

Table 1: Glass transition temperature and crosslink density data.

There is little variation in the thermomechanical T_g data for these sampled systems. Equally important, there is also little variation in the width of the tan δ peak, showing that the systems are homogeneous and the T_g data is consistent across ramp rates in these profiles. The glass transition temperature indicates the point where long-term chain mobility becomes more apparent across the system. For this to occur at similar temperatures for these samples, these systems likely have similar architectures and network characteristics.

To further compare the characteristics of these matrices, crosslink density for these materials were found using an equation that related the elastic storage modulus (E') in the rubbery plateau to the crosslink density (v_c),

$$v_c = E'/3RT$$

Where R is the gas constant and T is the temperature in Kelvin. The values for the crosslink density can be found in Table 1. It should be noted that the values are relative because the above equation is only quantitative for ideal rubbery systems with much lower crosslink densities than those of epoxies.

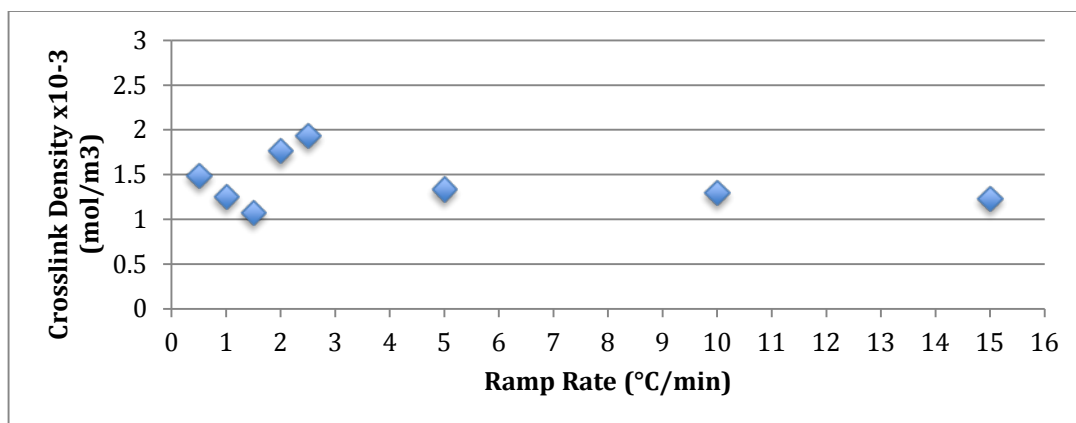


Figure 7: Crosslink density as a function of ramp rate during cure

There is little appreciable change in the crosslink density of these systems, and the changes seen can be attributed to noise that occurs from errors in sample preparation. Since the T_g of the samples is similar, it makes sense that the similarities carry into their crosslink density values. Since T_g occurs once chains have the energy to move, how closely they are packed to one another will impact the T_g value of the resulting thermoset network. Since the T_g and crosslink densities of the samples are similar, the connections between these chains and the degree of cure among these systems must also be similar. It is theorized that, since vitrification was still reached at the same temperature, the diffusion of reactive groups through the network was not hindered considerably by the varying heating ramp rates during cure.

3.3 Compression Testing

Compression testing is a mechanical testing process that allows for an analysis of the mechanical characteristics of a network as it would perform in industrial settings; In other words, the testing takes place in ambient conditions and therefore close to STP.

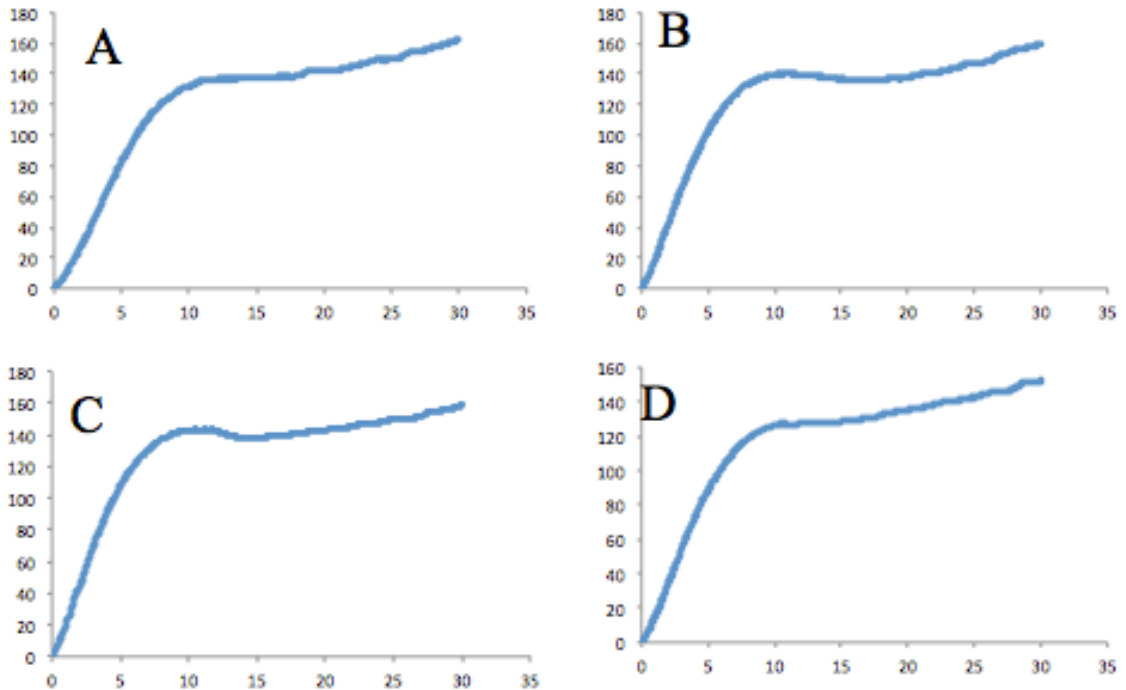


Figure 8: Compression data for 1 °C/min (A), 5 °C/min (B), 10 °C/min (C), and 15 °C/min. Axes are labeled stress vs. strain

For these materials, the stress vs. strain curves show that the materials show similar deformation properties across the different ramp rates for the materials. This indicates that the polymer chains are responding to mechanical deformation in similar manners regardless of how quickly the materials were taken to 180 °C.

Compression Data		
Ramp Rate °C/min	Modulus MPa	Yield stress MPa
0.5	2302.68±180	139.39±1.11
1.0	2070.02±254	138.53±3.11
1.5	2356.14±112	138.90±0.974
2.0	2155.92±244	137.66±3.37
2.5	2396.90±16	136.38±1.16
5.0	2531.38±239	139.41±1.52
10.0	2238.41±221	143.49±0.587
15.0	2483.03±637	127.33±7.37

Table 2: Compression data showing modulus and yield stress in Mega Pascals (MPa).

The modulus values showed similar behavior, with the materials yielding between about 127 and 143 MPa. The lathing process likely caused the some defects to arise in the samples and could have led to the variations seen in the yield stress data. The modulus of each sample shows similar characteristics of lying between about 2100 and 2500 MPa. A thermoset system's modulus is related to the network architecture in that a higher crosslink density will lead to a stiffer system. At the macroscopic scale, these systems exhibit similar deformation resistances as displayed in their modulus values; these is likely linked to homogenous networks across the sample sets, meaning that the ramp rate did not have a noticeable impact on how these materials responded to compression in ambient conditions.

Chapter 4: Conclusions

The final cure temperature and total cure time of epoxy-amine systems has been known have an effect on the final properties of these matrices due to limiting chemical events such as gelation and vitrification during cure.^{4,6} However, during the examination of the observable mechanical and thermomechanical properties of these epoxy-amine samples consisting of 4,4-DDS and DGEBA, no significant changes in the free volume hole size, T_g, modulus, or yield stress of these systems was observable when the heating rate during cure was varied significantly. The similarities may be caused by the post cure settings of the thermosets. In industry, a post cure is common and therefore these conditions were emulated in the laboratory. The 3 hours at 180 °C may have given the growing matrix enough time and energy to allow for the diffusion of monomer through the crosslinks of the system. This post curing would have a significant chance to ‘hide’ many of the differences in network architecture that would have been apparent across the system, such as dangling chain ends or more highly crosslinked microgels that could have been present. With the bulk of the material exhibiting homogeneous network attributes, the mechanical and thermomechanical properties exhibited by the samples did not differ largely across sample sets.

Chapter 5: Future Work

These 4,4-DDS/DGEBA epoxy-amine system consists of a difunctional epoxide monomer and tetrafunctional aromatic amine curative. Further research on how varying the functionality of epoxide resins by using systems such as TGAP and TGDDM (see Figure 1) while carrying the systems' cure rates would impact network architectures would allow for a different view on how giving the system a more defined epoxy-based character by increasing the amount of epoxide functional groups could lead to network differences.

Further, the amine curative used in this research aromatic in nature; the reactivity rates of the primary and secondary amine are significantly different.⁶ During network growth, the primary amines will react first and, after a certain amount is depleted, the secondary amines will begin reacting. Certain amine curing agents display similar reactivity ratios between the primary and secondary amines; these reactivity differences could impact the network in different ways upon heating rate variation during cure.

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