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## The Effect of Cure Rate on Glassy Polymer Networks

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The University of Southern Mississippi

The Effect of Cure Rate on Glassy Polymer Networks

by

Kristen Van de Voorde

A Thesis  
Submitted to the Honors College of  
The University of Southern Mississippi  
in Partial Fulfilment  
of the Requirement for the Degree of  
Bachelors of Science  
in the Department of Polymer Science

May 2016



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## Abstract

The formation of glassy polymer networks such as epoxy-amine systems may be altered by varying the temperature ramp rate that is used to cure the system. As a result, the physical and mechanical properties of the network may be changed. This work synthesized the epoxy resins diglycidyl ether of bisphenol A (DGEBA) with the amine curing agent 4,4-diaminodiphenyl sulfone (4,4'-DDS) from 35°C to 180°C using varying temperature ramp rates. Mechanical and structural properties of these samples were then analyzed to determine the effect the different temperature ramp rates had on the formation and properties of the thermoset matrix. These aspects were analyzed using Dynamic Mechanical Analysis (DMA), Differential Scanning Calorimetry (DSC) and real-time Fourier Transform Near-Infrared (NIR) Spectroscopy.

It was found that higher temperature ramp rates during the cure cause the epoxide function groups to be consumed more rapidly. Also, these faster rates create materials that are less homogenized and have a lower glass transition temperature.

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

## **Dedication**

To my mom, KK, dad, and sisters, Megan and Lauren, for their  
love and support.

## **Acknowledgements**

Firstly, I would like to thank my advisor, Dr. Wiggins, for being a fantastic teacher and mentor. The research I was able to do during my undergraduate years was a complete joy and I am thankful for the experience. Additionally, I would like to thank my graduate student Andrew Janisse. He was my first graduate student to work under and was always encouraging along the way.

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## **List of Abbreviations**

DGEBA- diglycidyl ether of bisphenol A

DGEBF- diglycidyl ether of bisphenol F

44DDS- 4,4'-diaminodiphenyl sulfone

DMA- dynamic mechanical analysis

DSC- differential scanning calorimetry

DOC- degree of cure

NIR- Near Infrared

## Chapter 1: Introduction

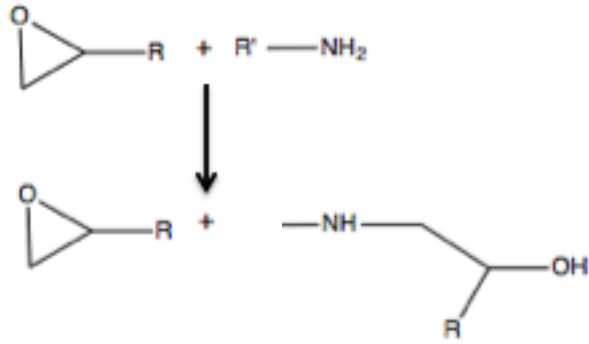
### *1.1 History of epoxy resins*

During the 1940s, the military began developing tough, lightweight materials to replace heavy metals in airplanes and rockets.<sup>1</sup> The first materials that were researched were glass fiber reinforced polymers (GFRP). However, these systems were too brittle at high temperatures for most real applications.<sup>1</sup> It was later discovered that dispersing short fibers in a light, lower strength matrix greatly increased the overall material's mechanical properties.<sup>1</sup> In the 1960s, scientists found that the concept of composites were the optimal material to be used in vehicles.<sup>1</sup> Composites were defined as a system created by mixing two heterogeneous phases: a fiber and a matrix.<sup>1</sup> Currently, matrices formulated from epoxy resins are the most frequently used materials in aerospace.<sup>2</sup> This is because they create tough, chemically resistant composites that are able to perform well over years of use.<sup>2</sup> Additionally, epoxy thermosetting resins are corrosion resistant and able to withstand high temperature environments.<sup>2</sup> Multifunctional epoxy monomers are cured with hardeners at high temperatures over an extended period of time to ensure full conversion.<sup>2</sup>

### *1.2 Epoxy-amine reaction*

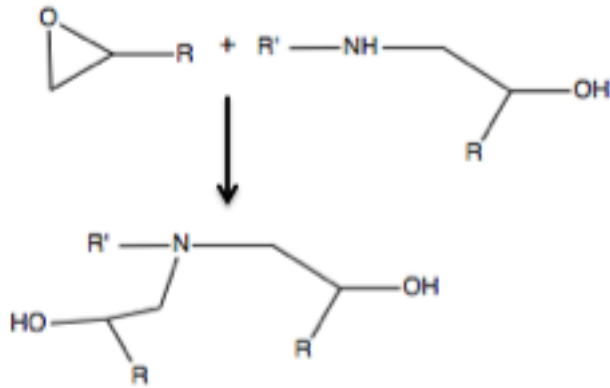
In a reaction to form an epoxy matrix that utilizes a primary amine hardener, the primary amine will react with an epoxied end group. This will transform the hardener to a secondary amine, where it will react later on in the reaction with another epoxide end group, and the product will contain a network of densely cross-linked tertiary amines and epoxies.<sup>3</sup> This reaction is illustrated in **Figure 1.1**. Primary amines have a substantially





**Figure 1.2:** Ring-opening addition reaction of an epoxide by a primary amine.

During this process, the kinetic polymer chains' molecular weights increase in a stepwise manner. This will continue until all of the monomers in the reaction are connected to another by at least one bond, and the molecular weight approaches infinity. After, crosslinking is the primary phenomenon, and it is mainly the secondary amines that take part. This progression is also a ring-opening addition process, and is depicted in



**Figure 1.3:** Ring-opening addition reaction of an epoxide by a secondary amine.

**Figure 1.3.**

Additionally, there are two phenomena that occur during crosslinking and polymerization: gelation and vitrification. These two phase transitions were studied by Lange *et al.* in 1994.<sup>6</sup> Gelation occurs when a thermosetting system reaches a particular

degree of conversion and crosslinking, and the sample transitions from a liquid to a gel, and this phase switch occurs at a single, non-reversible point known as the gel point. The gel point was defined using DMA on epoxy systems as the point where the  $\text{Tan } \delta$  of a sample was no longer dependent on the frequency. Vitrification occurs when a resin transitions from a gel to a glassy amorphous material. Unlike gelation, vitrification occurs over a gradual period. To identify this development in the epoxy samples, four criteria for vitrification were applied to dynamic mechanical analysis data: onset of frequency dependence on storage modulus, peak of  $\text{Tan } \delta$ , peak of loss modulus, and the end of frequency dependence on storage modulus.

The transition from polymerization to crosslinking is typically the gel point of a reaction. After gelation, the mobility of the polymer chains is partially limited, and the kinetics of the overall reaction decreases.<sup>7</sup> Vitrification occurs after a thermoset such as an epoxy-amine resin is highly cross-linked. The mobility of the polymer chains is severely restricted at this point, and the system then depends on diffusion to reach full conversion<sup>6</sup>.

### *1.3 Quantifying kinetics*

Because the transitions of epoxy-amine networks cause the system to change its  $C_p$  throughout the curing process, it is possible to use DSC to study the kinetics of the network formation. An epoxy network was tested at six different curing temperature ramp rates via DSC by Karkanis and Partridge in 2000.<sup>8</sup> It was found that at lower temperature ramp rates, epoxy-amine systems began their reactions at lower temperatures, and the systems that were cured slower had higher conversion rates over an allotted amount of time. This demonstrates that the cure rates do have an effect on

network formation. This method does not describe the kinetics of the different species involved within the reaction, but there are some conclusions that can be drawn from this research. High temperature ramp rates for curing epoxy-amine thermosets could potentially have two effects on the network formation. The high temperatures early in the reaction could allow the secondary amines to have similar reactivity ratios as primary amines. This would cause the reaction to form many crosslinks before all of the monomers had an opportunity to react. This early onset of crosslinking may sterically hinder the kinetics of chain extension. If the chain's mobility is greatly restricted before most of the reactive sites consume each other, most of the sample's conversion will be due to diffusion. This may produce a system with a low degree of cure.

The other possible effect that exposing the reaction to high temperatures early is vitrification. It is possible for a sample to have a phase transition from liquid to glass if the temperature of the reaction is rapidly brought about the sample's glass transition temperature ( $T_g$ ). Since vitrification causes restricted movement of the polymer chains, the resulting network would have a low crosslinking density as well.

To determine the specific kinetics of the epoxides, primary amines, and secondary amines, a method must be used that is able to calculate the chemical change of a sample while it is being cured. NIR-IR spectroscopy is capable of measuring the concentrations of specific function groups over a range of temperatures, and Mijovic *et al.* utilized this method in 1995 to study epoxy-amine networks.<sup>9</sup> The main focus of this research was analyzing the extent of the reaction over the time of the reaction. Several different samples were cured over a range of temperatures for a set period of time. However, all of the samples were cured at the same temperature ramp rate.



This method is capable of quantifying the concentrations of each functional group species throughout the duration of the cure. This is because IR spectroscopy utilizes the Beer-Lambert's law, which states:

$$A=\epsilon bc \quad (1)$$

In FT-IR spectroscopy, A is the absorption of a specific species,  $\epsilon$  is the molar absorptivity coefficient (a constant for a component at the wavelength and operating conditions for which it is determined), c is the concentration of the specific species, and b is the path length the optical light must travel through the sample. At any given wavelength and temperature, three of the four variables can be known, and the concentrations of a particular species can be monitored throughout the reaction. Unfortunately, experiments that study the thermal kinetics of a reaction via IR require a range of temperatures. As a result, to accurately calculate the concentration of a species throughout a thermo cure, the  $\epsilon$  value must be measured for each temperature over a range of frequencies.

#### *1.4 Analysis of Mechanical Properties*

The main reason that the epoxy-amine thermosetting resins have desirable properties for aerospace applications is a direct result of the high crosslinking density and the three-dimensional networks they form. The key aspect of studying the network formation at different temperature ramp rates is analyzing how it will affect the mechanical abilities and properties of the networks. Since the glass transition temperature is tied to many of a sample's mechanical properties, finding the T<sub>g</sub> via DMA will be the main method used in this study.

The T<sub>g</sub> of a thermoset provides an indication of the cross-link density of a sample. As the crosslink density is increased, the T<sub>g</sub> of a sample is shifted to higher temperature. Epoxy networks were tested for their crosslinking densities by Liu *et al.* in 2009.<sup>10</sup> The samples were characterized via DMA, and the crosslink densities were calculated using equation (1). In this equation  $\rho$  is crosslink density, E is the storage

$$\rho = E/3RT \quad (1)$$

modulus, T is the temperature 50°C above T<sub>g</sub>, and R is a constant. It was found that the epoxy networks that had lower crosslinking densities also had lower T<sub>g</sub>s. This is to be expected because lower cross-linked materials have a higher molecular weight in between crosslinks. This allows for more long-range molecular motions.

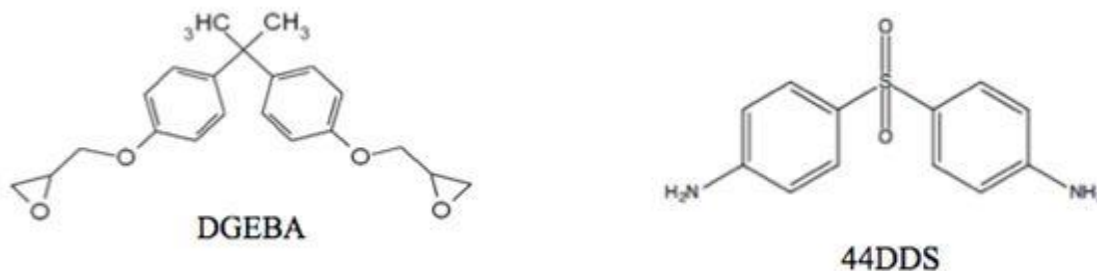
### *1.5 Epoxy Amine Resins in Aerospace*

The aerospace industry is currently producing planes that are comprised of more carbon fiber composites than metal. Composites are made up of two different components: fibers and a polymeric matrix. For aerospace applications, the matrix within the composites must have a high level of toughness. Cytec Technology Corporation patented a resin that consisted of DGEBA, DGEBF, and the curing agent was 44DDS. The thermoset resin that was produced was extremely tough and appropriate for aerospace applications.<sup>11</sup> These are the resins that will be examined in this study.

## **Chapter 2: Method**

This research focused on one epoxy-amine networks: Diglycidyl ether of Bisphenol (DGEBA) and the amine curative 4,4-diaminodiphenyl sulfone. EPON™ 825 is the DGEBA derivative that was reacted in this research, and it contains 175 g/equivalent of epoxy equivalent weight. The 44DDS monomer that was used in this

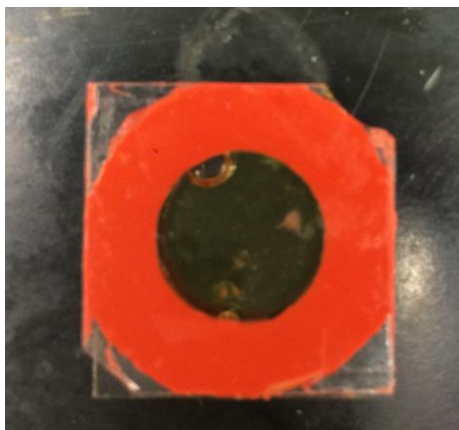
research had a 97% purity, and it has a molecular weight of 62.08. The amine curative was dried in a vacuum oven at 50°C for 24 hours. **Figure 2.1** illustrates the structures of the reactants.



**Figure 2.1:** Molecular structures of DGEBA and 44DDS.

### *2.1 Glassy polymer network preparation*

For each characterization method, a large sample batch was prepared. These batches were done by placing desired amounts of amine into an Erlenmeyer flask that was equipped with a vacuum fitting. A stoichiometrically equivalent amount of epoxy was then measured into the flask. The reactants were placed in a flask and mechanically stirred, and the flask was placed in an oil bath set to 80°C until the amine dissolves into the epoxy. When the characterization method for the batch is DMA or DSC, the sample were ready to be molded appropriately. When the characterization method for the batch is NIR, the batch was further heated to obtain optically clear samples. This was done by placing the reaction vehicle that contains the mixture under vacuum, and the oil bath was heated 5°C/5min until the oil bath reaches 120°C. The reaction was heated slowly to prevent gelation. The mixture then transitioned from a milky to clear coloration. At that point, the samples were ready to be molded appropriately, and **Figure 2.2** accurately depicts the ready sample.



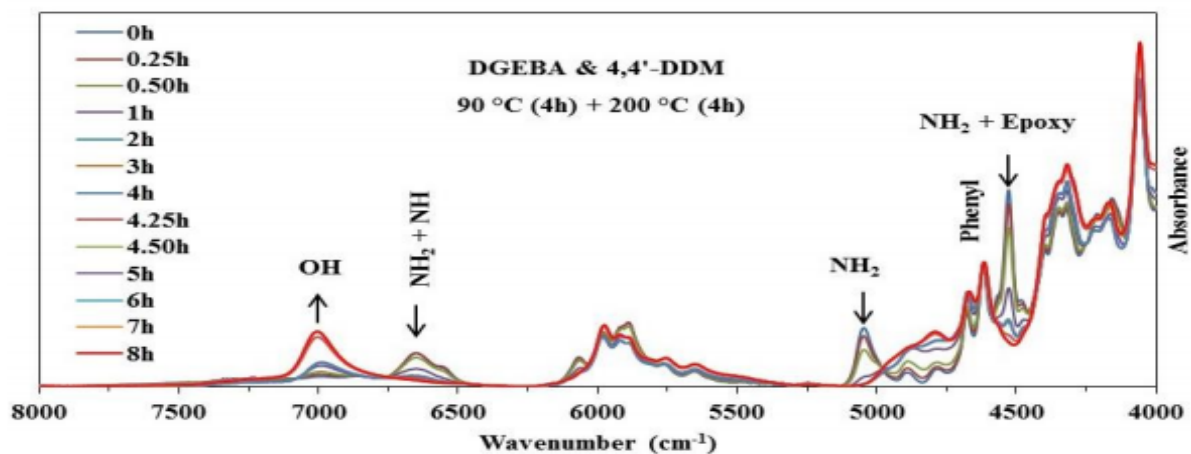
**Figure 2.2:** NIR spectroscopy sample that is fully prepped.

### *2.2 Near infrared spectroscopy (NIR spectra)*

NIR spectra was collected using a Thermo Scientific Nicolet 6700 FT-IR in transmission mode over the  $4000\text{-}8000\text{ cm}^{-1}$  range. A  $\text{CaF}_2$  beam splitter along with a white light and DTGS KBr detector was used. The samples were molded by placing the previously prepared mixture in between microscope glass slides, using a washer as a spacer. The washer was then sealed to the glass via silica sealant. Samples were then placed in the instrument, and the B-stage resins were cured at varying temperature ramp rates from  $35^\circ\text{C}$  to  $180^\circ\text{C}$  and a three-hour hold at  $180^\circ\text{C}$ . Every two minutes of the curing process, 16 scans at  $4\text{ cm}^{-1}$  will be obtained. There are five different temperature ramp rates that were examined in this research:  $1^\circ\text{C}/\text{min}$ ,  $5^\circ\text{C}/\text{min}$ ,  $10^\circ\text{C}/\text{min}$ ,  $15^\circ\text{C}/\text{min}$ , and  $20^\circ\text{C}/\text{min}$ . The raw data was then analyzed using two computer soft wares: Origin and Excel.

Once those samples were tested, the kinetics of the reaction were properly analyzed. Since the integration of the primary amine and secondary amine peaks in a NIR spectra are not isolated, as illustrated in **Figure 2.3**; the analysis of the kinetics for the four functional groups were done in a stepwise process. This was done by graphing the

concentration over time relationship for the hydroxyl groups because it is the only relevant peak that is isolated and can be integrated. The kinetics of the hydroxyl should be the inverse of the epoxy. After the consumption rate of the epoxy was found, the consumption rate of the primary amine can be calculated. This was done by integrating the peak at  $\sim 4500\text{cm}^{-1}$  that contains the primary amine and epoxy absorbencies. Subsequently, the concentration over time relationship was calculated, and the concentration at each time due to epoxy will be subtracted. The appearance and consumption of secondary amine was then found by integrating the peak at  $\sim 6700\text{cm}^{-1}$  that contains the primary and secondary amine absorbencies. Then, the concentration over time relationship was calculated, and the concentration at each time due to primary amine was subtracted.



**Figure 2.3:** NIR spectra of EPON 828 and 44DDM during a cure.

There were five different concentration versus time plots generated from this experiment for each network because each of the five different temperature ramp rates will generate reactions with different kinetics.

### *2.3 Dynamic mechanical analysis (DMA)*

A DMA Q-800 TA Instruments instrument was used to obtain dynamic mechanical properties of both of the networks at each of the five different temperature ramp rates. The samples previously prepared were cast using a silicone mold designed to mold bars with the dimensions 1.5mm x 5mm x 60mm. The mold was preheated at 100°C to allow for an easier casting process. The silicone mold was then cured in an oven from 35°C to 180°C with a three-hour hold at 180°C. Each batch was cured at the five different temperature ramp rates and each will be characterized via DMA. The instrument will be used in tensile mode at a frequency of 1 Hz from -125°C to 300°C at a ramp rate of 5°C/min.

DMA is able to determine the loss modulus, the storage modulus, the glass transition temperature, the full-width- half-maximum, and the cross-linking density.

### *2.4 Differential scanning calorimetry (DSC)*

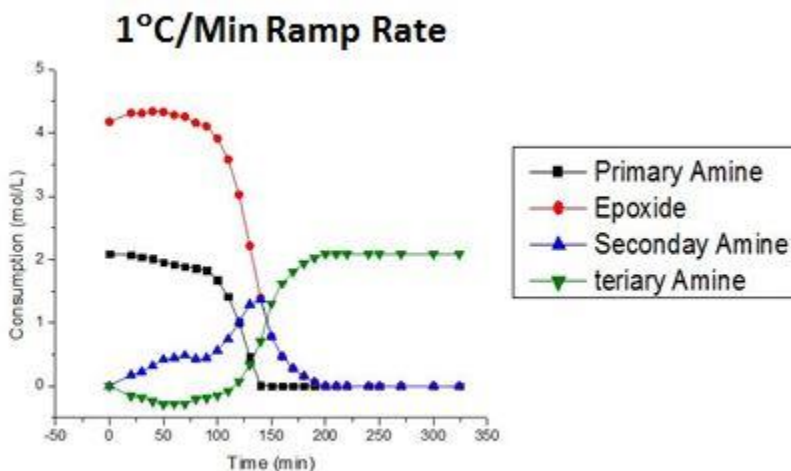
A TA Instrument Q200 DSC instrument was used to examine the endothermic and exothermic transitions each network has at each temperature ramp rate. The samples for this instrument were tested by placing 5 to 10 mg of the epoxy-amine system in DSC pans. Then the samples were tested ten different ways. Five of the samples were completely uncured prior to the test, and the instrument heated them at each of the ramp rates. This generated a large exothermic curve. The other five samples were all cured prior to the testing at the five temperature ramp rates previously used, and then the samples were tested. These exothermic curves generated were compared to the other set. This data was later analyzed to find the Degree of Cure (DOC).

DSC is able to analyze the network formation. By comparing the exotherm of each network, it is possible to determine which sample had a higher degree of cure: The larger the exotherm, the lower the DOC of the system.

### Chapter 3: Results and Discussion

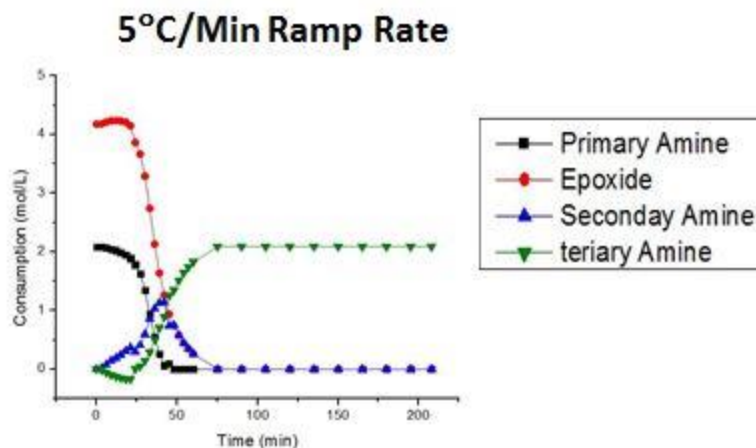
#### 3.1 Near infrared spectroscopy (NIR spectra)

Samples were prepared and tested using NIR, and the spectra was analyzed to obtain graphs that display the rates of consumption over time. **Figure 3.1** is the analyzed data of a DGEBA-44DDS sample that was cured at 1°C/min from 35°C to 180°C with a three hour hold at 180°C. The slope of the linear portion of the Epoxide consumption



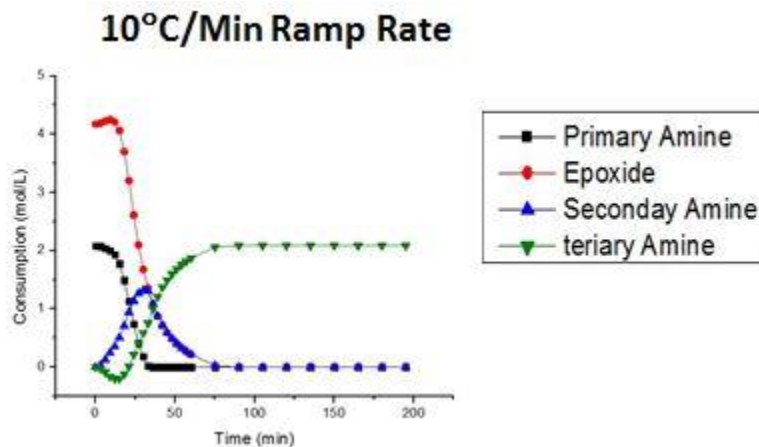
**Figure 3.1:** DGEBA-44DDS cured at a ramp rate of 1°C.

graph is -0.02, and the maximum peak of the secondary amine is 1.36685 mol/L. **Figure 3.2** is the analyzed data of a DGEBA-44DDS sample that was cured at 5°C/min from 35°C to 180°C with a three hour hold at 180°C. The slope of the linear portion of the epoxide consumption graph is -0.148, and the maximum peak of the secondary amine is



**Figure 3.2:** DGEBA-44DDS cured at a ramp rate of 5°C.

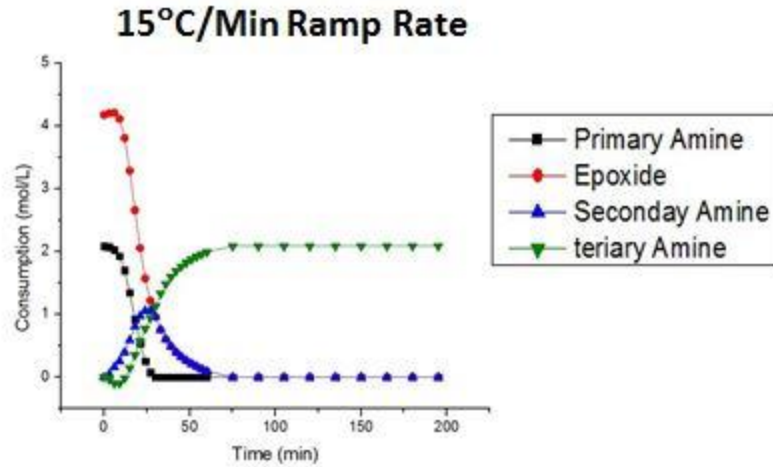
1.1373 mol/L. **Figure 3.3** is the analyzed data of a DGEBA-44DDS sample that was cured at 10°C/min from 35°C to 180°C with a three hour hold at 180°C. The slope of the



**Figure 3.3:** DGEBA-44DDS cured at a ramp rate of 10°C.

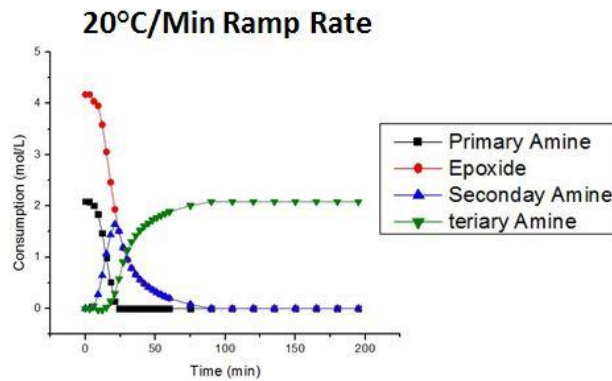
linear portion of the Epoxide consumption graph is -0.17, and the maximum peak of the secondary amine is 1.0610 mol/L. **Figure 3.4** is the analyzed data of a DGEBA-44DDS sample that was cured at 15°C/min from 35°C to 180°C with a three hour hold





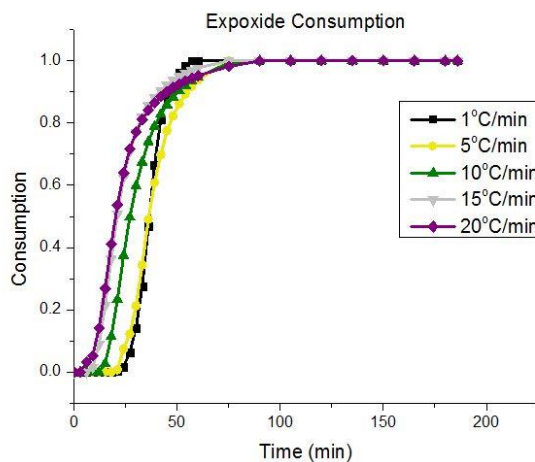
**Figure 3.4:** DGEBA-44DDS cured at a ramp rate of 15°C.

at 180°C. The slope of the linear portion of the Epoxide consumption graph is -0.17, and the maximum peak of the secondary amine is 1.0567 mol/L. **Figure 3.5** is the analyzed data of a DGEBA-44DDS sample that was cured at 20°C/min from 35°C to 180°C with a three hour hold at 180°C. The slope of the linear portion of the Epoxide consumption



**Figure 3.5:** DGEBA-44DDS cured at a ramp rate of 20°C.

graph is -0.22, and the maximum peak of the secondary amine is 1.64 mol/L. There is an obvious trend throughout the data that is depicted in **Figure 3.6**: The faster the

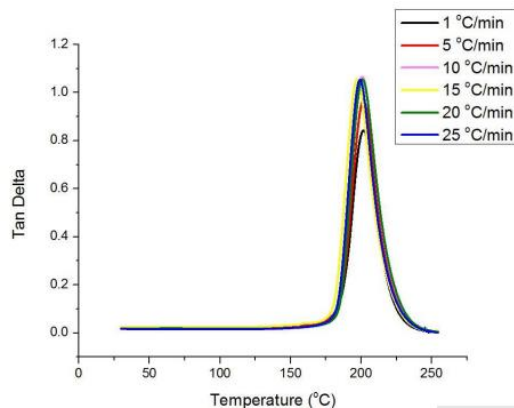


temperature ramp rate

**Figure 3.6:** All five of the different epoxide consumption rates measured.

during the cure, the faster the Epoxide is consumed in the reaction. This indicated that the faster the ramp rate the quicker the network is formed. Additionally, there is another steady trend in the data that deals with the maximum peak of the secondary amine. Almost over all, the faster ramp rates have a decreasing maximum secondary amine. This indicates that during the cures with faster ramp rates, some of the secondary amine reacts while the primary amine is still reacting.

### 3.2 Dynamic Mechanical Analysis (DMA)



**Figure 3.7:** Tan Delta peaks obtained via DMA.

Samples were prepared and tested using DMA. All of the Tan Delta peaks were plotted, and the glass transition temperatures, the volume crosslink density, and the full width half max were analyzed. The raw Tan Delta curves are depicted in **Figure 3.7** and the analyzed data is seen in **Table 3.1**. Over all, there was a shift in the glass transition

<b>Ramp Rate (°C/min)</b>	<b>T<sub>g</sub> (°C)</b>	<b>V<sub>c</sub> x 10<sup>3</sup> (mol/m<sup>3</sup>)</b>	<b>FWHM (°C)</b>
<b>1</b>	206	1.97	18.74
<b>5</b>	203	1.78	18.53
<b>10</b>	201	2.12	20.42
<b>15</b>	197	1.94	20.21
<b>20</b>	198	2.17	20.52
<b>25</b>	199	2.28	19.33

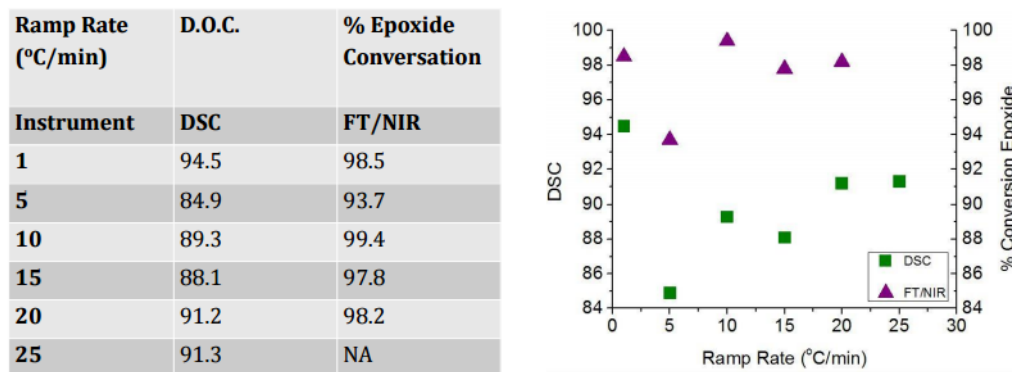
**Table 3.1:** Analyzed DMA data.

temperature. The higher the temperature ramp rate during the cure, the lower the glass transition temperature. Additionally, there was a trend that the higher the temperature ramp rates during cure, the larger the full width half max of the Tan delta curves. From this, we can infer that less homogenous systems are created when higher temperature ramp rates are used. However, there was no overall trend for crosslink density.

### 3.3 Differential scanning calorimetry (DSC)

DSC was used to analyze the DOC of the samples cured at the different temperature ramp rates. This method was preformed because most epoxy-amine kinetics are analyzed with method. The trend of the DOCs should math the trend of the percent of epoxide consumption measured through NIR spectroscopy. The data displayed in Figure

3.8 compared the DOCs measured via DSC to the percent epoxide consumption measured through NIR spectroscopy.



**Figure 3.8:** DOC measured via DSC.

It was noted that the methods do depict a similar trend; for most of the different cure ramp rates, there is no fluctuating DOC or percent epoxide conversion. As a result, it is noted that by changing the cure profile of these samples, there was not change in DOC or epoxide functional group consumption.

#### Chapter 4: Conclusion

The same DGEBA/44DDS epoxy-amine system was cured at varying temperature ramp rates. Through NIR spectroscopy, the kinetics of the system was studied, and the consumption of four functional groups was analyzed. During this experiment, it was noted that at higher temperature ramp rates during the cure led faster consumption of epoxide function. Additionally, at the higher temperature ramp rates, the secondary amine reacted earlier on while the primary amine was still reaction. From this data, it is inferred that changing the cure rate does alter the formation of the epoxy-amine system tested.

The cured samples were then tested through DMA. The analyzed data from this method shows that higher temperature ramp rates during the cure result in a material with

a lower glass transition temperature as well as a less homogeneous system. However, there was no correlation between the temperature ramp rates during the cure with the crosslink density. Also, the DOCs measured via DSC show the same trend as the percent epoxide conversion measured via NIR spectroscopy.

## **Chapter 5: Future Work**

The next step in this research is replacing DGEBA with DGEBF. These experiments will examine the effect of the substituent groups on the kinetics of the reaction. This is important because DGEBF is slightly less stable than DGEBA, and this could possibly change the trends noted in this work.

Moreover, this future work would include testing 33DDS instead of 44DDS. This would test the effect of a different isomer, and could potentially change the trends noted in this work.

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