Molecular Toughening of Epoxy Networks

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Abstract
Molecular Toughening of Epoxy Networks
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In the area of high performance composites, epoxies are the most widely used polymer matrix due to their favorable properties including: high modulus, high glass transition temperature, and easy processability which includes low shrinkage, no volatiles, and high adhesion to fillers and fiber reinforcement. The excellent mechanical properties arise from the highly cross-linked structure of the cured epoxy resins; however, their cross-linked structure leaves them with poor resistance to crack propagation.

Typically, the toughness of epoxies has been improved through the use of additives, often a phase-separating rubber. Additives can cause problems during composite processing, such as non-uniform dispersion of the toughening agent, so it is advantageous to increase the toughness of the neat resin as much as possible. Most methods for innate toughening of epoxies have relied on deviating from stoichiometry, which causes other properties to suffer. In this research systematic changes in molecular structure are investigated to determine how they affect the network properties, especially fracture properties, of neat epoxies.

Bimodal amine distributions were made using polyetheramines of various molecular weights. When cured with a rigid epoxy, the resulting networks, compared to single-distributions networks, had similar bulk cross-link densities but broader glass
transitions and lower modulus due to local network heterogeneity. The fracture behaviors were altered but the toughness did not improve. Polydisperse epoxy distributions, with dispersity indices ranging from 1.8 to 10.7, when cured with a linear amine, had no noticeable impact on the network properties.

Linear epoxies and blends of linear epoxies cured with rigid amines yield similar behaviors as those seen with linear amines. All structural variations can be collapsed onto unified curves by relating either the flexible volume fraction or the cross-link density to the maximum in tan δ.

Local heterogeneity in the cross-link density can be taken advantage of when coupled with a secondary toughening phase. Glass beads functionalized with epoxy groups and reacted with a high molecular weight polyetheramine increased the fracture toughness more than glass beads in homogeneous network or a heterogeneous network with the shorter chains at the bead-matrix interface.
Chapter 1: Introduction and Background

1.1 Motivation and Scope

Epoxies are a widely used class of polymers, and some aspects of them have been extensively researched; however focus in other areas has been lacking. A Web of Science search yields almost 107,000 results for epoxies; including toughness in the search parameters reduces the results to nearly 7000. Searching for impact strength instead of toughness reduces the results to 4000. If high strain rate is instead searched for, the number of results is less than 800. Looking closely at the search results reveals that some aspects of epoxy networks have either been cursorily or not explored. Many of these results, especially for impact toughness and high strain rate, are focused on glass or carbon reinforced composites rather than the neat epoxy. When non-composite networks are investigated, they are most frequently toughened systems. This implies that limited research has been done on neat epoxies, especially outside the quasi-static testing regime, even though real world impacts often happen at higher rates.

The motivation for this dissertation is to improve fracture properties of epoxies through molecular structural changes. This work focuses on understanding the effects of controlled structural changes to epoxy networks, with the intent to improve fracture properties yet retain other desirable properties such as modulus and glass transition temperature as to retain use in composite systems. To accomplish this, several objectives have been established.
1.2 Research Objective and Specific Aims

Closely examining controlled variations of molecular structure and the impacts of network properties on epoxy toughness is the first step to optimizing high rate performance of epoxy resins.

Specific Aims:

1. Determine whether bimodal distributions in either the epoxy or amine can provide enhanced properties compared to resins containing single distributions
2. Characterize the structural effects of different epoxies and amines while maintaining a constant glass transition temperature or cross-link density
3. Apply knowledge gained from #1 and #2 to a toughened epoxy system for enhanced toughness
4. Develop a methodology for notching thermoset fracture specimens that yields more consistent results than the commonly used razor scoring method

Related work is investigating these changes at high strain rates [2].

1.3 Background

1.3.1 Introduction

Epoxy resins are widely used but find their main uses in five major areas: coatings, adhesives, electronic insulation, construction, and composites. Over half of all epoxies are used in coatings but epoxy composite materials are also a significant area [3]. In the area of high performance composites, epoxies are used more often than any other resin [4]. Epoxy composites are used extensively in both commercial aircraft, such as the
Boeing 787 Dreamliner which is 50% composites by weight, as well as in military aircraft. The F-22 fighter is approximately 25 wt% composites, although the US Air Force has used epoxy composites as structural parts since 1969 [6]. Epoxy composites also find use in helicopter rotor blades: the composites provide vibration control as well as weight savings over their aluminum counterparts.

Epoxy composites also find use in space applications where their weight savings is coupled with their ability to have a tailored coefficient of thermal expansion (CTE). Given the wide temperature range an object may experience, −100 – 100 °C, a CTE as close to zero is desirable. In more terrestrial applications epoxy composites find use in automotive components, such as leaf springs, although their use is mainly limited to high performance vehicles where the cost of carbon fiber-reinforced epoxy can be justified [6]. Other uses for epoxy composites include medical devices such as prosthetics, sports equipment such as golf clubs and bicycle frames as well as fishing poles [6]. Again the main advantage is weight reduction over their metallic counterparts.

There are several reasons epoxy resins are so widely used in the composite industry. These include: high modulus, high glass transition temperature ($T_g$), and easy processability which includes low shrinkage, no volatiles, and high adhesion to fillers and fiber reinforcement. The excellent mechanical properties arise from the highly cross-linked structure of the cured epoxy resins; however, their cross-linked structure leaves them with poor resistance to crack propagation. This poor toughness is often remedied through the addition of a secondary phase.
1.3.2 Epoxy Background and Chemistry

The global market for epoxy resins was 1.15 million metric tons in 2000 [7] and is estimated to reach over 3 million metric tons by 2017 [8]. Worldwide, approximately 75% of epoxy resins are derived from diglycidyl ether of bisphenol A (DGEBA) whose structure is shown in Figure 1.1A [7]. The value of \( n \), the number of additional repeat units per molecule, can range from <0.1 for liquid epoxies to over 35 for Type 10 solid epoxy resins. Solid epoxies are widely used in coatings while the lower molecular weight liquid epoxies tend to be used where their low viscosity eases processing, such as flooring and composite applications. Solid epoxies have longer backbones giving more distance between cross-links, resulting in improved toughness [9]. The additional repeat units also incorporate additional hydroxyl functionality that can be reacted with isocyanates or other cross-linkers. High molecular weight epoxies are made by two processes: the taffy process and the fusion process. The taffy process is called such due to the taffy-like appearance of high molecular weight epoxy during the process. The process uses epichlorohydrin, bisphenol A, and a stoichiometric amount of sodium hydroxide; it generates an epoxy distribution with both odd and even numbers of repeat units. The fusion process generates epoxy with mostly even numbers of repeat units by combining DGEBA with bisphenol A. The fusion process is more widely used in commercial manufacturing [7].

Novolacs are type of multifunctional epoxy resin whose epoxy functionality increases with increasing molecular weight. They are commercially important as their multifunctionality leads to higher cross-link density and better thermal and chemical resistance over DGEBA-type epoxies; however, their cost is approximately double that of
DGEBA epoxies [7]. The two main types of novolacs are phenol or cresol based; shown in Figure 1.1B.

Figure 1.1: Structure of A) DGEBA and B) phenol based novolac epoxy.

Epoxies can be characterized by the $n$ value, but they are more often characterized by their epoxy equivalent weight (EEW) which is the molecular weight of the molecule normalized by the number of epoxy groups per molecule.

Epoxies can react with a variety of compounds to produce thermoset materials. Amines are most commonly used as epoxy hardeners but other possible reagents include acid anhydrides and cyanate esters. Lewis acids, typically boron trifluoride complexes, can be used as a catalyst to achieve epoxy homopolymerization [10]. Ionic liquids have also been used to cure epoxies [11].
Three main reactions describe the cure of amine cured epoxy resins [12-14]: primary amine-epoxy addition, secondary amine-epoxy addition, and hydroxyl-epoxy (etherification), all shown in Figure 1.2.

Other reactions are also possible, including epoxy homopolymerization, although for some epoxies, this does not occur significantly below 180 °C [15]. For the cure temperatures used in this work, the etherification and homopolymerization reactions can be neglected [14, 16]. Reactions A and B are autocatalytic, being catalyzed by hydroxyls which are either present initially on the epoxy, as impurities such as water, or are formed during cure.

For most applications, a stoichiometric balance of one epoxy group per amine hydrogen is desired. For practical applications the stoichiometric masses of each
component can be calculated used the epoxy’s EEW and the amine’s amine hydrogen equivalent weight (AHEW) as shown in equation 1.1:

\[
\frac{AHEW \times 100}{EEW} = M_{amine} \text{ per } 100 \text{ g of epoxy}
\]

where \( M_{amine} \) is the mass of amine.

1.3.3 Fracture Mechanics

Polymers can fracture either in the linear elastic or the nonlinear elastic plastic regimes. Epoxies well below their \( T_g \) often obey linear elastic fracture mechanics (LEFM) while near and above \( T_g \) and in cases of extreme toughness, they fail nonlinearly. The following review will be restricted to LEFM. Information on nonlinear fracture mechanics, including the J integral and crack-tip-opening displacement (CTOD) can be found elsewhere [17].

One approach to fracture mechanics is built on the energy criterion which states a crack will grow once the energy available for crack growth is sufficient to overcome the resistance of the material. It was first proposed by Griffith [18] and later developed by Irwin [19] into the present form, where \( G \) is the energy release rate and at the moment of fracture is the critical energy release rate, \( G_c \). For an infinite flat plate with an internal crack of length \( 2a \):

\[
G_c = \frac{\pi \sigma_f^2 a}{E}
\]

1.2

where \( \sigma_f \) is the failure stress and \( E \) is the tensile modulus.

The other approach is the stress-intensity approach [17]. An element near the tip of a crack has in-plane stresses described by equations 1.3-1.5:
\[
\sigma_{xx} = \frac{K_I}{\sqrt{2r\pi}} \cos\left(\frac{\theta}{2}\right) \left[1 - \sin\left(\frac{\theta}{2}\right) \sin\left(\frac{3\theta}{2}\right)\right]
\]

\[1.3\]

\[
\sigma_{yy} = \frac{K_I}{\sqrt{2r\pi}} \cos\left(\frac{\theta}{2}\right) \left[1 + \sin\left(\frac{\theta}{2}\right) \sin\left(\frac{3\theta}{2}\right)\right]
\]

\[1.4\]

\[
\tau_{xy} = \frac{K_I}{\sqrt{2r\pi}} \cos\left(\frac{\theta}{2}\right) \sin\left(\frac{\theta}{2}\right) \cos\left(\frac{3\theta}{2}\right)
\]

\[1.5\]

where \(r\) is the radial distance from the crack tip, and \(K_I\) is a constant. The subscript \(I\) refers to the mode of failure. The three basic modes of failure are: I: opening; II: in-plane shear; III: out-of-plane shear and are illustrated in Figure 1.3. If \(K\) is known, then the stress field around the crack tip can be calculated. If a material fails locally under a critical combination of stress and strain, then \(K_I\) become \(K_{Ic}\), the critical stress intensity.

Solutions for \(K_{Ic}\) are given in the form:

\[
K_{Ic} = \frac{P_c}{B\sqrt{W}} f\left(\frac{a}{W}\right)
\]

\[1.6\]

where \(P_c\) is the load at fracture, \(B\) is the sample thickness, \(W\) is the sample width and 

\(f\left(\frac{a}{W}\right)\) is a geometry specific function dependent on the crack length, \(a\), and \(W\).

For plain strain, \(K_{Ic}\) and \(G_{Ic}\) are related by:

\[
G_{Ic} = \frac{K_{Ic}^2 \left(1 - \nu^2\right)}{E}
\]

\[1.7\]
For a sharp crack, the stress at its tip, $\sigma_t$, is given by:

$$\sigma_t = 2\sigma \sqrt{\frac{a}{\rho_c}}$$

where $\sigma$ is the applied stress, $a$ is the crack length and $\rho_c$ is the tip radius. As the tip curvature decreases, the stress at the tip increases, illustrating the stress concentrating effect of cracks or flaws. Mathematically LEFM predicts infinite stress at a sharp crack tip. In reality the stresses are finite as the radius of the crack tip is finite. Local plastic deformation around the crack tip further reduces the stress concentration. Some methods for increasing fracture toughness increase the amount of plastic deformation in the vicinity of the crack tip; however, if extensive yielding occurs, LEFM no longer apply and nonlinear fracture mechanics must be considered.

### 1.3.3.1 Homogeneous Toughening Methods

Some of the earlier methods for increasing toughness involved altering the epoxy/amine ratio away from stoichiometry. Selby and Miller varied the epoxy/amine ratio, by weight, from 100:20 to 100:40, with a stoichiometric ratio of 100:27 and showed
that fracture toughness increased by over 60% [20]. Other work showed similar results [21-23] though a consequence of deviating from stoichiometry is a decrease in other properties, especially the T_g [24].

More recent work was based on systematically altering the cross-link density of epoxy networks. Crawford and Lesser controlled the network properties by using mixtures of similarly sized amines containing two, three, or four amine hydrogens to alter the T_g and the cross-link density; aromatic and aliphatic amines were separately used [25]. The curing agent, whether aromatic or aliphatic had no effect on the rubbery modulus of the resins. They also found that for resins cured with mixtures of aliphatic mono- and difunctional amines, the fracture behavior changed from brittle to ductile as the molecular weight between cross-links (M_c) increased. As the M_c increased, T_g and yield strength decreased [26]. In another study by Crawford and Lesser the relationship between crosslink density and T_g for DGEBA with aliphatic amines was investigated [27]. They determined that both the cross-link density as well as the cross-link functionality influences the T_g; modifications to existing models were proposed to account for the cross-link functionality. Their work only considered the theoretical crosslink density and did not consider the possibility of different blends having the same crosslink density. Mayr, Cook, and Edward attempted to vary the cross-link density while altering the chemistry as little as possible [28-29]. Their work used varying ratios of a mono-amine, either aliphatic or aromatic, and its dimeric analogue, while maintaining overall stoichiometry. For both amines, the compressive yield stress increased with increasing crosslink density. When plotted versus T_g-T, the yield stresses for both aromatic and aliphatic cured resins fell on a common line.
The work of Grillet et al. showed that the structure of the network can affect the fracture properties. Samples were made using five aromatic amines with different backbone stiffness. This resulted in networks with $T_g$s above 180 °C, similar crosslink densities, but fracture toughness values that differed by a factor of three [30]. The lowest $T_g$ resin did have the highest fracture and impact toughness but a slight $T_g$ difference ($<5$ °C) does not account for the large difference in fracture toughness values. Also, the $T_g$ and crosslink density were not directly proportional to each other.

Pascault et al. summarize most experimental results as: chemical structural effects influence the yield stress of epoxies predominately through $T_g$ changes and for unmodified epoxies, the yield stress has an inverse relationship with toughness [31], though that does not explain the subtler structural effects as seen by Grillet.

1.3.3.2 Microvoid Toughening

Simulations have shown that the formation of microvoids in highly cross-linked systems can increase the toughness of the system through strain hardening [32-33]. The microvoids are formed by rearrangement of the molecules, with no bonds being broken. If the molecules are restricted to only forming bonds in tetrahedral arrangements, then the microvoids cannot form and no strain hardening occurs.

Sharifi et al. recently reported increased ductility and toughness in an epoxy-amine network by modifying the topography of an epoxy-amine network through the use of solvent induced voids [34]. When epoxy-amine networks are cured in the present of a solvent, the network forms around pockets of the solvent. After cure, the solvent can be extracted, leaving small voids in network. These voids do not alter the $T_g$, Young’s modulus or density of the networks, but the ductility was greatly increased.
1.3.3.3 Heterogeneous Toughening Methods

Limited success in toughening epoxies through homogeneous means led researchers to focus on heterogeneous toughening methods, such as adding a dispersed secondary phase. Broadly speaking the secondary phase can be broken into two categories: hard and soft particles. Hard particles include glass [35-37], silica [38-40], alumina [41-43], clays [44], and other fillers [45]. Soft particles can either be preformed [35, 40, 46-48] or formed in situ as the polymer cures. Rubbers such as carboxyl-terminated butadiene-acrylonitrile (CTBN) are soluble in the liquid epoxy and phase separate as the epoxy cures with the size of the resulting CTBN particles depending upon the speed of the cure and solubility of the CTBN, among other factors [9, 49-54]. Mixtures of hard and soft particles have also been used [39-40, 55-57] as have thermoplastics and copolymers [58-63].

1.3.3.4 Toughening Mechanisms

In untoughened epoxies, the main mechanism for toughness is plastic deformation. The addition of a secondary phase introduces other mechanisms that increase the toughness. These include: crack pinning [55], crack deflection [64-66], particle debonding [35, 66], cavitation [67], and void growth [53].

Crack pinning assumes that a growing crack can be slowed by rigid well-bonded hard particles [55]. When a growing crack encounters these hard particles it bows out between particles, changing the shape of the crack front, forming secondary cracks, and requiring additional energy to continue growing. Crack deflection results in increased surface roughness as the crack front twists and tilts around solid particles [64-66]. A rough surface contains more surface area and therefore requires more energy during its
formation than a smooth one. The tilting, twisting crack is subject to mixed-mode loading [64]. Cavitation is the result of stress causing elastomeric particles to rupture. The particles then relax into the cavities, giving the appearance of hole growth [67] or the holes/voids can grow [53]. The act of cavitation is thought to be less important than the subsequent hole growth [68-69]. Similarly particles can debond from the matrix and the resulting holes can continue to grow [35, 66, 70].

1.4 Thesis Outline

This thesis is divided into seven chapters:

Chapter 1 establishes the motivation for this work and presents the overarching aims of the research. A brief background on epoxy chemistry is presented along with a brief background on linear-elastic fracture mechanics. Homogeneous and heterogeneous toughening mechanisms in thermosets are also reviewed.

Chapter 2 focuses on two characterization methods: dynamic mechanical analysis and fracture testing. Dynamic mechanical analysis (DMA) is a commonly used analytic technique for polymers, yielding modulus and T_g data; however, the modulus results can be greatly dependent upon both the sample size and the clamp type used. A literature review of common DMA usage is presented along with experimental data that culminates with sample size and clamp type recommendations. The fracture testing portion addresses Aim #4, exploring several methods for initiating the starting crack.

Chapter 3 focuses on Aim #1 by presenting experimental data of networks containing bimodal distributions of linear polyetheramines. Polyether diamines with
three molecular weights are blended to give intermediate average molecular weights; these amines are cured with DGEBA.

Chapter 4 continues to address Aim #1 with experimental data for polydisperse epoxies. Five different high molecular weight DGEBA-based epoxies are blended with a low molecular weight one to yield blends with similar EEWs. All blends are cured with a single polyetheramine.

Chapter 5 addresses Aim #2, presenting experimental data for several structural variations. These variations include two types of linear epoxies, aromatic and cyclic amines. In addition it combines results from Chapters 3, 4, and 5.

Chapter 6 addresses Aim #3. The epoxies are toughened with either plain or epoxy functionalized glass beads. The functionalization allows the bead-matrix interface to be controlled which in turn influences the fracture toughness.

Chapter 7 concludes this dissertation with a summary of key findings and conclusions and suggests avenues of future work.
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Chapter 2: Characterization Techniques

2.1 Introduction

While many techniques are used throughout this work, this chapter focuses exclusively on two techniques: dynamic mechanical analysis (DMA) and mode I fracture testing. DMA is a common and versatile analytical technique used to characterize polymers and a wide variety of sample shapes and sizes can be accommodated through the use of different clamps. Several ASTM standards address DMA testing [1-4], but none with any specificity regarding sample dimensions. Here the affects that sample dimensions have on the DMA results are explored and property-dependent dimensional guidelines are recommended. On the other hand, sample dimensions for mode I fracture toughness are well defined in an ASTM standard [5]; however there are three options for generating the starter crack. Multiple methods for generating the initial crack are investigated with the desired result of reducing the scatter that is often found in fracture toughness data.

2.2 Dynamic Mechanical Analysis

DMA is often described as applying an oscillatory force to a sample and measuring the sample’s response to that force. In a perfectly elastic material, the phase angle or lag, $\delta$, between the force and the displacement is $0^\circ$ and for a viscous material it is $90^\circ$. For viscoelastic materials, such as polymers, there is some intermediate delay between displacement and the application of the force. In DMA measurements, this is
broken into in-phase and out-of-phase components, resulting in the calculation of storage
or elastic moduli (\(E'\)) and loss, or viscous, moduli (\(E''\)) from a measured stiffness [6].
Additionally the ratio of the storage to loss modulus is the \(\tan \delta\) and is one of the basic
properties measured by DMA; some early instruments only recorded \(\tan \delta\) [7]. From
these basic measurements, other properties such as glass transition temperature (\(T_g\)), beta
and other relaxation temperatures, gelation, and vitrification can be determined. General
types of DMA tests include temperature sweeps, frequency sweeps, studies of curing
behavior or vitrification, stress-relaxation and creep-recovery, among others [7].

![Figure 2.1: Sketches of A) three point bending, B) dual cantilever, C) single cantilever, and D) tension fixtures.](image)

Testing can be done in many geometries, including tension, compression, shear,
three point bending, dual and single cantilever. Three geometries that are commonly
used to test polymers are the three point bending (3pt), dual cantilever (DC) and single
cantilever (SC) clamps. Tension is also commonly used but mainly for polymeric films. Sketches of each are shown in Figure 2.1. The three point bending clamp allows the sample to move freely during testing while the cantilever fixtures clamp the sample at both ends. The middle is also clamped for dual cantilever. The clamping of the sample introduces a shearing component to the distortion which increases the stress required to produce a given displacement [7]. The testing span is fixed by the clamp geometry for the 3pt and DC clamps, but for the SC, the distance between the two clamps must be measured, as there can be slight lateral movement of the moveable clamp.

Several ASTM standards address polymer characterization by DMA. These include: D4065: Dynamic Mechanical Properties: Determination and Report of Procedures [4], D 5023: Dynamic Mechanical Properties: In Flexure (Three-Point Bending) [1], D 5026: Dynamic Mechanical Properties: In Tension [2], and D5418: Dynamic Mechanical Properties: In Flexure (Dual Cantilever Beam) [3]. The general DMA standard, D4065, is purposely vague on sample dimensions “due to numerous types of dynamic mechanical instruments,” but does mention that thick specimens of low modulus materials or thin specimens of high modulus materials may be required. Standards D5026 and D5418, for tension and DC, respectively, leave specimen size even more ill-defined:

Any rectangular specimen (representative of the material being tested and within the fixturing capabilities of the test equipment) may be used as long as it is clearly described in the test report. [2]

The 3pt standard, D5023, is the only one that addresses specimen dimensions with any specificity, in stating that a span-to-thickness ratio of 16 (tolerance +4, -2) is typical,
similar to the ratio required in ASTM D790 – the standard covering flexural modulus testing [8]. While all of these standards mention that a significant decrease in $E'$ will occur signifying the glass transition temperature, none of them address what effect the generally 3 orders of magnitude decrease in modulus will have on the measurements.

Since the standards do not favor specific geometries for specific tasks, there is no consensus on which geometry to use for polymers. The DMA instrument manufacturers do suggest sample dimension ranges for given geometries [9], but do not discuss how a three order of magnitude modulus change through the glass transition can affect DMA measurements. Numerous researchers favor the 3pt bend geometry [11-23], other favor the DC geometry [24-32], and others favor the SC geometry [33-71]. However, Duncan and others claim that the 3pt bend geometry is best suited for high modulus materials, such as metals, ceramics, and highly filled thermosetting polymers that show little change in modulus throughout the test [6, 9]. Duncan also suggests that the SC and DC clamps are better suited for characterizing materials through the glass transition [6], although SC is preferred, especially for materials with high thermal expansion [9]. In DC the clamped ends can cause a build-up of either tension or compression due to thermal stress, resulting in erroneous modulus results [6]. Duncan states that DC is better suited for low expansion or highly oriented materials [6].

The tension clamp is frequently used for polymer films; however, making a thin uniform film of many thermosetting polymers can be difficult. The inherent high stiffness of the tension sample can require high applied force to achieve the desired strain. As many DMAs are limited to 10-20 N [6], this limits the thickness of a tensile specimen. Duncan recommends thickness of $< 20 \mu$m for glassy polymers and $> 100 \mu$m
for rubbery ones. These thicknesses can prove problematic for filled or phase-separating systems, especially if the filler is on the order of microns in size.

### 2.2.1 Background

Judging by numerous published results, TA Instruments is a popular manufacturer of DMA machines with the Q800 being their current model and the 2980 being the similar previous model. Yet, the analysis below is valid for virtually any DMA instrument or manufacturer although the governing equations will differ. The TA Instruments Q800 and 2980 models have stiffness ($K_3$) sensitivity ranges of $10^2$-$10^7$ N/m with a maximum applied force of 18 N. From the raw force, amplitude and phase angle measurements, storage and loss stiffness values are computed which are converted into storage and loss moduli by equations 2.1-2.4 for 3pt, DC, SC, and tension experiments.

A clamping correction factor, $F_c$, eq. 2.5, is calculated from finite element analysis.

\[
E_{3pt} = K \frac{L^3}{6l} \left[ 1 + \frac{6}{10} \cdot (1 + \nu) \left( \frac{t}{L} \right)^2 \right]
\]

\[
E_{DC} = \frac{K}{F_c} \frac{L^3}{24l} \left[ 1 + \frac{12}{5} \cdot (1 + \nu) \left( \frac{t}{L} \right)^2 \right]
\]

\[
E_{SC} = \frac{K}{F_c} \frac{L^3}{12l} \left[ 1 + \frac{12}{5} \cdot (1 + \nu) \left( \frac{t}{L} \right)^2 \right]
\]
\[ E_{\text{TEN}} = K \cdot \frac{L}{A} \]

\[ F_c = 0.7616 - 0.02713 \cdot \sqrt{\frac{L}{t}} + 0.1083 \cdot \ln \left( \frac{L}{t} \right) \]

where \( t \) is the sample thickness, \( w \) the sample width, \( L \) is the span for 3pt and SC and one half the span of the DC, \( I \) the geometric moment \( \left( \frac{1}{12} t^3 W \right) \), \( A \) the cross-sectional area, and \( v \) is Poisson’s ratio.

Since stiffness is size dependent, a geometry factor (GF) can be calculated, equations 2.6, 2.7, 2.8, and 2.9.

\[ GF_{3pt} = \frac{L^3}{48I} \left[ 1 + \frac{12}{5} \cdot \left( 1 + v \right) \left( \frac{t}{L} \right)^2 \right] \]

\[ GF_{DC} = \frac{1}{F} \left[ \frac{L^3}{24I} + S \cdot (1 + v) \frac{L}{A} \right] \]

\[ GF_{SC} = \frac{1}{F} \left[ \frac{L^3}{12I} + 2S \cdot (1 + v) \frac{L}{A} \right] \]

\[ GF_{\text{TEN}} = \frac{L}{A} \]

where \( A \) the cross sectional area, \( F \) is a clamping factor (nominally 0.9 ), and \( S \) is a shearing factor (nominally 1.5 ). The equations for the tension clamp are mathematically simplest, as the small area requires no end-effect correction factors. For both the
modulus and GF calculations of the other clamps, the thickness has the greatest influence as it appears cubed in the denominator and can vary greatly between samples. While L in each is also cubed, its influence is minimized as the lengths are determined by the clamp and do not vary much from sample to sample. The GFs coupled with the modulus calculations and the stiffness limits can be combined into an operating window determined by sample size and modulus, with a maximum modulus of 3 TPa [9]. These operating windows are shown in Figure 2.2. For DMA instruments from other manufacturers, the force and stiffness limits and the exact geometry calculations may differ, but are conceptually the same as above. As such, all DMAs have an operating window and sample thickness plays a large role in determining whether a given sample is within this operating window.
Figure 2.2: Operating windows (solid lines) for the three clamps along with the glassy (5°C) and rubbery modulus measured at both constant, 3.2 mm, thickness (S-T = 5 for SC, 6 for 3pt and 11 for DC) and constant span-to-thickness (S-T = 11). The 3pt samples that prematurely stopped recording data are not included.

Also dependent upon the sample geometry is the strain induced by a given deformation. For these instruments, the strains can be calculated by eq. 2.10, 2.11, or 2.12, where $\delta$ is the amplitude of deformation, $t$ the thickness, $\nu$ the Poisson’s ratio, and $L$
is one half the span for 3pt bend and DC geometries, but \( L \) is the full span for the SC geometry and the sample length for tension.

\[
(\varepsilon_{\text{max}})_{3pt} = \frac{6 \cdot \delta \cdot t}{2L^2 \left(1 + \frac{6}{10}(1 + \nu) \left(\frac{t}{L}\right)^2\right)}
\]

\[
(\varepsilon_{\text{max}})_{DC\&SC} = \frac{3 \cdot \delta \cdot t \cdot F_c}{L^2 \left(1 + \frac{12}{5}(1 + \nu) \left(\frac{t}{L}\right)^2\right)}
\]

\[
(\varepsilon_{\text{max}})_{\text{TEN}} = \frac{\delta}{L}
\]

While the elastic moduli measured by DMA do not often agree with those from other mechanical testing methods [72], ideally they are equivalent and independent of DMA manufacturer. It has been reported that DMA results are affected by clamp type [72], oscillation amplitude, sample alignment, and sample thickness [73].

Lee-Sullivan and Dykeman investigated thickness, amplitude, and alignment affects on polycarbonate in a three-point bending clamp [73] on a TA Instruments 2980 DMA. With increasing amplitude, the modulus slightly increased. For a given amplitude, their samples with span-to-thickness ratios of 11 and 17 had similar moduli, while those with a span-to-thickness ratio of 33 were higher. For the lower span-to-thickness samples, all but the 25 \( \mu m \) amplitude, 4.5 mm thick samples were within 7% of the reference modulus, with most of the samples having errors less than 5%. The slight increases in moduli with increasing amplitude can best be explained by approximating
the sinusoidal displacement as a triangular wave [74]. The average strain rate can then be calculated as:

$$\dot{\varepsilon} = 2\varepsilon \cdot f$$  \hspace{1cm} 2.13

where $\dot{\varepsilon}$ is the strain rate, $\varepsilon$ is the maximum strain and $f$ is the frequency. Doubling the amplitude and hence the maximum strain at constant frequency, yields a strain rate equivalent to doubling the frequency at constant amplitude. A similar effect would have been seen if they increased the frequency from 1 to 8 Hz. Polymer moduli are frequency dependent, a fact exploited by time-temperature superposition (TTS) [75]. While TTS generally spans decades of frequencies, even a minor increase in strain rate will cause an increase in modulus, such as that seen by Lee-Sullivan and Dykeman. As the increases in amplitude were minor, so were the modulus increases, with the results remaining very similar to the reference modulus [73]. If the displacement is too small; however, the test may not be in bending mode but rather a mix of bending and torsion as the sample “settles” on the clamp rather than bends, resulting in incorrect modulus values [6]. The higher modulus and error of the 25 µm amplitude samples can be attributed to this. For the 33 span-to-thickness samples, moduli errors of 12-17% were reported. A span-to-thickness (S-T) ratio range of 10:1 to 32:1 is recommended by the manufacturer [9]. It is not unexpected that span-to-thickness ratios outside the recommended range have incorrect moduli.

Deng et al. tested filled and unfilled epoxy on a 2980 DMA using 3pt, DC, and SC clamps and compared the results to those from flexural and tensile tests [72]. The results from the 3pt clamp matched the flexural data well but the DC and SC results did not. Unfortunately, they did not specify the sample thicknesses for many of the tests. In
the one test where thicknesses were specified, the SC test had a span-to-thickness ratio of 6 while the 3pt test had one of 17. This imbalance of the ratios explains the mismatch between modulus results for that test. Contrary to Lee-Sullivan and Dykeman’s results, Deng et al. saw decreasing modulus for 3pt tests with increasing amplitude. It is impossible to reconcile these two observations with the available information; however, Lee-Sullivan and Dykeman did show that poor sample alignment can decrease modulus results for three point bending tests [73].

For TA Instruments’ DMAs, the clamp dependent operating windows are defined by stiffness sensitivities of the instruments. A sample’s stiffness is a function of both modulus and sample geometry. As the modulus can change substantially with increased temperature, careful choice of sample size is necessary to ensure the measured stiffness stays within the operating window. Lee-Sullivan and Dykeman and Deng et al. showed that thickness, span-to-thickness, and oscillation amplitude all affect DMA results, but they only investigated room temperature, i.e. glassy modulus effects.

This work builds off general guidelines to specify optimum geometries and dimensions to obtain accurate DMA results in the glassy region through the rubbery plateau for thermosetting polymers on a specific instrument. As all clamps have their advantages and disadvantages, in this work we characterize five epoxy-amine networks on the 20 mm 3pt, the 35 mm DC, and the 17.5 mm SC clamps and compare the results, focusing on a glassy and rubbery modulus values, as well as the glass transition temperature ($T_g$). The 20 mm 3pt clamp was chosen over the more commonly used 50 mm clamp to limit sagging of the sample at higher temperatures. We performed two comparisons: the first maintaining a constant thickness across samples of a given resin,
approximately 3.2 mm, as was done in Deng et al. [72], and the second maintaining a constant span-to-thickness ratio, approximately 11:1. For an independent modulus value, ASTM D790 [8] was followed to obtain flexural modulus values for all the polymers at room temperature (23°C). A limited comparison of rubbery modulus values between the SC clamp with two sample thicknesses and the tension clamp was also made.

2.2.2 Experimental

Five epoxy-amine resins were examined. All used high purity diglycidyl ether of bisphenol A (DGEBA), Epon 825 from Momentive, with an epoxy equivalent weight of 175 g/mol. This was cured with five different amines: 4,4’-methylenebiscyclohexanamine (PACM) from Air Products, 1,3-phenylene diamine (PDA) and 1,3-diaminopropane (DAP) from Sigma-Aldrich, and polyetheramine diamines Jeffamine D230 and Jeffamine D400 from Huntsman. All reagents were used as received and their structures are shown in Figure 2.3. Resins will be identified by their amine component.
The DGEBA was heated to 50-60°C and degassed to remove any crystals or residual volatiles. A stoichiometric amount of amine was added, with two molecules of DGEBA per molecule of amine. The mixtures were thoroughly mixed using an ARE 250 Thinky centrifugal mixer (Thinky Corp., Japan), then degassed under vacuum. Resins were poured into an aluminum mold, previously coated with release agent Frekote 55-NC (Henkel), and cured at 80°C for two hours. After curing the samples were removed from the mold before post curing according the conditions shown in Table 2.1 using cited references to obtain ideal cure.

Table 2.1: Post cure conditions

<table>
<thead>
<tr>
<th>Resin</th>
<th>Post Cure Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>PACM</td>
<td>2 h at 160 °C [76]</td>
</tr>
<tr>
<td>PDA</td>
<td>2 °C/min to 225 °C + 20 minute isotherm, slow cool</td>
</tr>
<tr>
<td>DAP</td>
<td>8 h at 150 °C + 2 h at 200 °C [77]</td>
</tr>
<tr>
<td>D230</td>
<td>2 h at 125 °C [78]</td>
</tr>
<tr>
<td>D400</td>
<td>2 h at 125 °C [78]</td>
</tr>
</tbody>
</table>
DMA specimens were cast as bars with approximate dimensions of 70 mm x 12.7 mm x 3.5 mm. A Sanford surface grinder (Rahway, NJ) was used to machine the samples to the required thicknesses. For all samples, both sides were ground; grinding was performed after the post cures. For DC tests, the samples were machined to approximately 60 mm x 12.7 mm x 3.2 mm. For SC and 3pt testing, the samples were machined to approximately 35 mm x 12.7 mm x 3.2 mm for the constant thickness tests, yielding two samples per original bar. For the constant span-to-thickness ratio, the thicknesses were 1.55 mm and 1.8 mm for SC and 3pt, respectively.

For the D230 only, in addition to the above samples, another set of samples consisting of two thicknesses of SC samples and a tension specimen were also prepared. The SC samples were prepared as above while for the tension sample was cured on a glass microscope slide coated with Frekote NC-55; additional glass slides were affixed to the slide with double-sided tape, creating a “well” approximately 1 mm deep to contain the resin. The well was capped with another slide to ensure a flat, uniform sample. The resin was then cured as described in Table 2.1. The resulting tension sample was approximately 1 mm in thickness and was cut to approximately 25 mm x 4.5 mm x 1 mm. The sample was lightly sanded to remove any trace of release agent, but otherwise the thickness was unaltered.

All samples were tested on a TA Instruments Q800 DMA, and the testing parameters are summarized in Table 2.2. After a ten minute equilibration step at 0 °C, the temperature was increased at 2 °C/minute to 250 °C. For most tests the oscillation
amplitude was set at 7.5 \( \mu \text{m} \) with a frequency of 1 Hz. Two samples per clamp geometry were tested. For DC and SC measurements, the clamps were tightened to 8 in-lb using a torque wrench. The 3pt clamp is a tensioning clamp, meaning that an additional static force is required to maintain a positive force on the sample throughout the oscillation. The force track was set to 125\%, meaning the static force is 125\% of the dynamic force required for the oscillation, as recommended for general applications.

The tension clamp is also a tensioning clamp and the same force track as for the 3pt tests was used. The clamps were tightened to 3 in-lb, as recommended for film samples [9] and the same sample was tested twice. The first run was oscillated at 1 Hz with 0.02\% strain, and second also at 1 Hz but with 0.05\% strain. For both samples, after a ten minute equilibration step at 50 °C, the temperature was increased at 2 °C/minute to 150 °C. The above-ambient starting temperatures were used as only the rubbery modulus was of interest in these tests; additionally starting at an elevated temperature reduced the possibility of reaching the instrument’s force limit or the sample slipping in the clamps.

Flexural moduli were measured at room temperature (23 °C) in accordance with ASTM D-790 procedure B. Samples with approximate dimensions of 127 mm x 12.7 mm x 4.5 mm were cut from cast sheets; the thicknesses were unaltered after curing.
Table 2.2: Testing parameters and nominal dimensions.

<table>
<thead>
<tr>
<th>Clamp</th>
<th>Thickness (mm)</th>
<th>Span (mm)</th>
<th>Span-to-Thickness Ratio</th>
<th>Amplitude (µm)</th>
<th>Peak Strain (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DC</td>
<td>3.2</td>
<td>35</td>
<td>11</td>
<td>7.5</td>
<td>0.020</td>
</tr>
<tr>
<td>SC</td>
<td>3.2</td>
<td>17*</td>
<td>5.3</td>
<td>7.5</td>
<td>0.021</td>
</tr>
<tr>
<td>SC</td>
<td>1.55</td>
<td>17*</td>
<td>11</td>
<td>12</td>
<td>0.018</td>
</tr>
<tr>
<td>3pt</td>
<td>3.2</td>
<td>20</td>
<td>6.3</td>
<td>7.5</td>
<td>0.033</td>
</tr>
<tr>
<td>3pt</td>
<td>1.8</td>
<td>20</td>
<td>11</td>
<td>12</td>
<td>0.032</td>
</tr>
<tr>
<td>Tension #1</td>
<td>1.1</td>
<td>14.7</td>
<td>13</td>
<td>2.9</td>
<td>0.020</td>
</tr>
<tr>
<td>Tension #2</td>
<td>1.1</td>
<td>14.7</td>
<td>13</td>
<td>7.3</td>
<td>0.050</td>
</tr>
</tbody>
</table>

*Nominally the span was 17.5; however the “as measured” values were closer to 17

2.2.3 Results

The flexural moduli of the epoxy-amine samples are shown in Table 2.3. The moduli range between 2500 MPa and 3000 MPa and most strongly depend on the amine with the Jeffamine and PDA hardeners producing the higher moduli while the PACM and DAP produced the lower moduli. The reason behind this is not entirely clear but current theories indicate that packing density is the dominant factor, and these results are consistent with literature findings [79-81].

The storage moduli from the DMA results were normalized by the flexural modulus to determine the amount of error as a function of sample geometry and sample dimensions. Figure 2.4 shows the room temperature normalized modulus for all resins on the three clamps. The DC clamp is the only one that matched the flexural modulus well, being within 90% of the flexural modulus in all cases. The 3pt clamp performed the worst, ranging from 53 to 81% of the flexural modulus. The SC clamp was intermediate; recording values 82-89% of the flexural modulus. If the span-to-thickness (S-T) ratios of these samples are considered, the DC is the only one with a ratio greater than 10.
(approximately 11). The ratios for the SC and 3pt are 5-6 and 6-7, respectively. It is surprising that the SC and 3pt moduli were so different given their similar S-T ratios. While the moduli were different, other properties were the same. The \( T_g \)s, taken to be the peak of the loss modulus curves, were similar regardless of clamp type, as shown in Figure 2.5. On a given clamp for a given resin, the standard deviation in \( T_g \)s ranged from 0.0 to 0.6 °C. For the same resin across all clamps, the largest difference between averages was in D230 with almost 5 °C difference between the SC and 3pt \( T_g \)s; other samples had differences of < 2 °C.

Table 2.3: Flexural moduli of the resins (ASTM D790) tested at room temperature (23°C).

<table>
<thead>
<tr>
<th>Resin</th>
<th>Flexural Modulus (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PACM</td>
<td>2520 ± 30</td>
</tr>
<tr>
<td>PDA</td>
<td>2980 ± 20</td>
</tr>
<tr>
<td>DAP</td>
<td>2600 ± 20</td>
</tr>
<tr>
<td>D230</td>
<td>2970 ± 20</td>
</tr>
<tr>
<td>D400</td>
<td>2920 ± 50</td>
</tr>
</tbody>
</table>
Figure 2.4: Normalized room temperature moduli with constant (3.2 mm) thickness samples (S-T = 5 for SC, 6 for 3pt and 11 for DC).

Figure 2.5: $T_g$s of resins with constant thickness samples (S-T = 5 for SC, 6 for 3pt and 11 for DC).
An S-T ratio of 11 resulted in DC moduli very similar to the flexural moduli, therefore, that ratio was chosen for constant S-T studies for the bending/cantilever geometries. Because the strain is a function of sample dimensions (eq. 2.10-2.12), the amplitude was increased to 12 µm for the thinner SC and 3pt samples to maintain similar maximum strains compared to the constant thickness samples. For SC and DC samples the strains were approximately 0.02% while they were approximately 0.03% for the 3pt bending samples, well within the linear elastic regime. These strains are similar to the lower amplitude (25-50 µm) samples of Lee-Sullivan and Dykeman.

When a constant S-T ratio is maintained, the modulus values are all very similar to the flexural modulus, as shown in Figure 2.6. In all cases the measured values were within 9% of the flexural moduli. Averaged over all resins, the DC samples were within 6%, SC within 5% and 3pt within 2% of the flexural moduli. Yet, generally the 3pt bend samples had the largest standard deviations likely due to some slippage of the sample within the clamp. The Tg's were again very similar (Figure 2.7), although with slightly more variation than in the constant thickness samples. For a specific resin and clamp, the standard deviations ranged from 0.0 to 1.6 °C, a slightly greater range than for the constant thickness samples. Between clamps of a given resin, all samples had differences between the highest and lowest Tg's of at least 2.2 °C, again slightly greater than the constant thickness samples. With the small sample sizes it is difficult to determine whether the Tg differences are significant; however, the constant span-to-thickness SC samples consistently have the lowest Tg's. These are the thinnest samples and most likely have the lowest Tg due to reduced thermal lag.
Figure 2.6: Normalized moduli of the resins tested at a constant span-to-thickness ratio (11).

Figure 2.7: Tgs of resins with constant span-to-thickness ratios.
Matching a room temperature flexural modulus while giving a consistent $T_g$ is important; however, one of the advantages of DMA experiments is measuring the modulus as a function of temperature, including, for thermosetting polymers, the rubbery region, the area above the $T_g$.

In the rubbery region, other differences between the clamps and sample geometry become obvious. The theory of rubber elasticity is often used to give insight into the cross-link density of thermosetting networks, even though it strictly applies to polymers with low cross-link densities and may not give completely accurate cross-link density measurements for highly cross-linked epoxies [82]. Nonetheless, numerous researchers have used it as a measure of cross-link density and it seems to show good trends for sample sets with similar chemistries [83-84]. The theory of rubber elasticity relates a modulus above $T_g$ to the cross-link density, $\nu_{XL}$, through eq. 2.14 where $R$ is the gas constant and $T$ is the absolute temperature.

$$\nu_{XL} = \frac{E'}{3RT}$$  \hspace{1cm} 2.14

If $\nu_{XL}$ is assumed to be a constant, reflecting the chemical cross-links in a system, then with increasing temperature, the modulus must also increase.

Figure 2.8 and Figure 2.9 show the rubbery regions for PDA and D400, respectively for both the constant S-T (8A and 9A) and constant thickness samples (8B and 9B). These two resins are the highest and lowest $T_g$ resins tested and are representative of the observed trends for all five resins. Depending on the test fixture and sample geometry several conflicting conclusions about $\nu_{XL}$ could be drawn. The SC and
3pt samples with low S-T (Figure 2.8B and Figure 2.9B) appear to adhere to eq. 2.14, with a slight increase of modulus with increasing temperature. The constant span-to-thickness SC results are almost constant for the PDA (Figure 2.8A), but are actually slightly decreasing throughout the rubbery region, while the D400 results (Figure 2.9A) are clearly decreasing. While for the DC results with both span-to-thickness ratios, the rubbery modulus continually decreases, giving the appearance that the polymer is continuously softening. The near-constant and decreasing moduli could suggest that additional terms are needed for eq. 2.14, such as those accounting for non-Gaussian chain behavior, steric interactions, or entanglements [85]. Additionally for the 3pt samples with constant S-T, the machine was unable to measure moduli below approximately 100 MPa. The sample did not break, but it appears that the moveable clamp lost contact with the sample as it went through its Tg. All 3pt constant S-T samples exhibited similar behavior, often right after the peak in the loss modulus. In some cases data collection resumed at higher temperatures. This could, perhaps, be remedied through alternate choices of amplitude and force track values; however, this was not investigated in this work.
Figure 2.8: Storage modulus of PDA tested on the three clamps with A) constant span-to-thickness and B) constant thickness.

Figure 2.9: Storage modulus of D400 tested on the three clamps with A) constant span-to-thickness and B) constant thickness.
Two factors can contribute to these conflicting rubbery behaviors that were not significant in the glassy region: thermal expansion and sample stiffness. Compared to metals and semiconductors, polymers have thermal expansion coefficients generally an order of magnitude larger [86]. For thermosets the thermal expansion coefficient increases more after the $T_g$ [75, 87-88]. Thermal expansion of the length is not an issue for the 3pt clamps, as the sample is free to expand, retaining a constant sample span; however, for the SC and DC clamps, expansion is limited by the clamped points, potentially resulting in tension, compression, or sagging along the length of the sample. Contraction at sub-ambient temperatures is not significant, given that 0 °C was the lowest temperature used. From room temperature, where the samples were loaded, to 0 °C, using expansion data described in Chapter 3, the D230 contracted 0.15% while the D400 contracted 0.18%. At higher temperatures, 50°C above $T_g$, D230 expanded 1.9%, while D400 expanded 1.6%. Extrapolating to 250 °C, the upper test limit here, expansion was 3.9% for D230 and 4.3% for D400. Length changes for these resins are listed in Table 2.4 based on spans of 17 and 35 mm for SC and DC respectively. Lateral movement of the moveable clamp limits errors from the expansion in SC. While using the SC clamp, lateral movement of -0.17 mm was measured as a sample cooled to -100 °C. Lateral movement due to sample expansion was not measured; however, the clamp without a sample loaded was observed to shift laterally up to 1 mm in response to gentle manual pressure.

With expansion in DC, which has three clamped points, it is impossible to correct the sample’s span. If the center clamp moves in response to expansion on one side, the other side of the sample becomes compressed or buckles. Equal expansion on either side
would result in the sample compressing or sagging on both sides. Simply put, the expanding sample has no place to go, resulting in erroneous modulus values [6]. Therefore, we contend that the DC cannot accurately measure the rubbery modulus of rigid thermosets because it cannot fit the behavior described in eq. 2.14. Yet, we presume that DC could be used if the samples are clamped at elevated temperatures, but this procedure introduces hazards to the process and is more complex than a standard DMA temperature sweep, and in fact, no evidence of this type of run has been found in the literature.

<table>
<thead>
<tr>
<th>Resin</th>
<th>Length Change at 0 °C (mm)</th>
<th>Length Change at T_g+50 °C (mm)</th>
<th>Length Change at 250 °C (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SC</td>
<td>D230</td>
<td>-0.026</td>
<td>0.323</td>
</tr>
<tr>
<td></td>
<td>DC</td>
<td>-0.053</td>
<td>0.665</td>
</tr>
<tr>
<td>SC</td>
<td>D400</td>
<td>-0.031</td>
<td>0.272</td>
</tr>
</tbody>
</table>

While expansion along the length spells doom (is detrimental to) for the DC, expansion in the other directions will affect measurements for the other clamps as well. In addition to expansion, Poisson’s ratio, \( \nu \), changes for thermosets above their T_g. In the glassy region \( \nu = 0.35 \) is commonly used while \( \nu = 0.5 \) is common in the rubbery region [89-92]. In this work \( \nu = 0.35 \) was used for best comparison to the flexural measurements. Equations 1 and 3 can be used to create ratios of the modulus of expanded, rubbery samples compared to the initial, glassy room temperature samples, assuming isotropic expansion, shown in eqs. 2.15 and 2.16.
where % is the percent expansion. Both results are width independent and the results are shown in Figure 2.10 as a function of percent expansion. In most cases, the modulus corrected to expanded dimensions is less than those calculated from initial dimensions, up to 15% less for a 3pt specimen with 4% expansion and rubbery $\nu$. The exceptions are for thick SC samples with expansion of 0-1%, and a rubbery $\nu$, i.e., samples that go through their $T_g$ relatively near the starting temperature. These conditions may apply to D230 and D400 near their $T_g$s. Those resins experience 0.9 and 0.5% expansion, for D230 and D400 respectively, going from 0 °C to their $T_g$s [78]. Poisson’s ratio of other epoxy networks has been reported to rapidly approach 0.5 as temperature approaches $T_g$ [89-92]. For resins that experience a small amount of expansion before reaching their $T_g$, the corrected moduli would be higher than the recorded; however the change in modulus is less than 1%.

While SC does have a stronger dependence on thickness than 3pt, overall it is affected much less by sample expansion and an increasing Poisson’s ratio. This, however, does assume isotropic expansion. The clamps on the SC will prevent isotropic
expansion in the vicinity of the clamps which will affect the corrections of Figure 2.10; however, this analysis also assumes that the 3pt samples do not deflect under their own weight. Figure 2.11 shows the positions at which the oscillations occur for the SC and 3pt PDA and D400 samples shown in Figure 2.8B and Figure 2.9B. As the temperature increases, the oscillation position decreases for the 3pt samples, with a small peak around $T_g$. This drop in position is indicative of sagging of the sample, introducing error, whereas the SC position is more constant, although somewhat noisy above $T_g$. The poor accounting for thermal expansion and sagging in 3pt, account for the difference in modulus seen in Figure 2.8B and Figure 2.9B. Figure 2.10 and Figure 2.11 reinforce the statement that the SC is the preferred clamp above the $T_g$ [6].

![Figure 2.10: Ratios of moduli from expansion-corrected dimensions with $\nu = 0.5$ to those from initial dimensions with $\nu = 0.35$ at various sample thicknesses.](image)
The second parameter that becomes significant above $T_g$ is sample stiffness. As mentioned previously, the DMA operating window is partially defined by the stiffness sensitivity of the instrument. In the glassy region, samples, almost independent of geometry, generally have sufficient stiffness, but in the rubbery region, stiffness and sample size can play an important role. Thin samples (i.e. high span-to-thickness ratio samples), such as those previously shown to best match glassy modulus data, can have a very low stiffness in the rubbery region; low enough, in fact, to be outside the sensitivity of the instrument. Table 2.5 shows the minimum measured stiffness values for each resin and clamp type and Figure 2.2 shows the $5 \, ^\circ C$ modulus for each resin as well as the lowest measured rubbery modulus values in the operating windows for each clamp; the 3pt samples that prematurely stopped recording data are not included in the figure.
Clearly, all glassy data for all three geometries fall well within the instrument sensitivity window. The D230 and D400 for SC with S-T = 11 had values outside the sensitivity range of the instrument, but all of the SC S-T = 11 samples are very near the edge of the operating window and exhibited the same rubbery behavior (i.e. decreasing modulus). On the other hand, the SC samples with S-T = 5 had values within the operating window and exhibited the slightly increasing modulus with temperature in the rubbery region as expected. The rubbery DC samples were within the sensitivity range, similar to that of the SC S-T = 5 samples. This shows that the likely reason that the dual cantilever samples produce erroneous results in the rubbery region is not the sensitivity of the instrument; it is due to the non-straight sample shape as a result of sample buckling due to the three clamping points.

Table 2.5: Minimum measured stiffness (N/m)

<table>
<thead>
<tr>
<th>Resin</th>
<th>Constant Thickness (3.2 mm)</th>
<th>S-T = 11</th>
<th>Constant Thickness (3.2 mm)</th>
<th>S-T = 11</th>
<th>Constant Thickness (3.2 mm)</th>
<th>S-T = 11</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3pt</td>
<td>DC&lt;sup&gt;b&lt;/sup&gt;</td>
<td>SC</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Constant Thickness (3.2 mm)</td>
<td>S-T = 6</td>
<td>Constant Thickness (3.2 mm)</td>
<td>S-T =11</td>
<td>Constant Thickness (3.2 mm)</td>
<td>S-T = 5</td>
</tr>
<tr>
<td>PACM</td>
<td>3093</td>
<td>2861</td>
<td>680</td>
<td>362</td>
<td>2660</td>
<td>208</td>
</tr>
<tr>
<td>PDA</td>
<td>4061</td>
<td>1623</td>
<td>1526</td>
<td>671</td>
<td>3442</td>
<td>327</td>
</tr>
<tr>
<td>DAP</td>
<td>3510</td>
<td>1540</td>
<td>1176</td>
<td>858</td>
<td>1866</td>
<td>239</td>
</tr>
<tr>
<td>D230</td>
<td>359&lt;sup&gt;a&lt;/sup&gt;/1802</td>
<td>4094</td>
<td>271</td>
<td>621</td>
<td>945</td>
<td>34</td>
</tr>
<tr>
<td>D400</td>
<td>1721</td>
<td>6794</td>
<td>498</td>
<td>455</td>
<td>874</td>
<td>35</td>
</tr>
</tbody>
</table>

<sup>a</sup>this sample showed unusual rubbery behavior so the minimum stiffness for both samples are presented

<sup>b</sup>many DC samples broke, leading to scatter in minimum stiffness

As mentioned, the instrument has a published sensitivity limit of 100 N/m; however this could be optimistic or perhaps only valid for a pristine instrument. For a
working/used instrument, perhaps stiffness in the 2-300 N/m range are also outside the sensitivity limits. To determine whether stiffness limitations affect the apparent rubbery behavior, samples of D230 were tested in the tensile geometry. The tension geometry maintains a high stiffness as well as has the ability to explicitly account for length changes due to expansion, eliminating the previously mentioned causes for artifacts in the rubbery region.

Figure 2.12A shows the results of the D230 tension samples (S-T = 14), along with SC and 3pt samples; the minimum stiffness for these samples are shown in Table 2.6. Both tension samples show a gradual increase in the rubbery modulus, similar to the thicker (S-T = 6) SC sample along with Figure 2.8B and Figure 2.9B and also in agreement with equation 2.11. As before the 3pt sample also agrees with eq. 2.11 but yields a lower modulus than the SC, but also lower than the tension samples.

There is an offset in T_g between the tension compared to the SC and 3pt samples; however, this is due to different thermocouple placement, different thermal lag or a combination thereof. The thermocouple was not adjusted for the tension clamp and the tension has a much smaller sample size, both of which could account for the lower apparent T_g. If the tension samples are shifted to match the T_gs of the other samples, as shown in Figure 2.12B, then the tension samples perfectly overlap the thicker SC samples.

In general, the samples showing a gradual increase in modulus in agreement with eq. 2.11 have stiffness greater than 870 N/m, while those showing a decreasing rubbery modulus have stiffness less than 330 N/m. This shows that the continuously dropping rubbery modulus is an artifact of insufficient sample stiffness and that the effective lower
sensitivity limit is higher than the ideal 100 N/m. In addition the agreement between the thicker SC samples and the tension samples suggests that the 3pt geometry under-measure the modulus in the rubbery region.

Table 2.6: Measured minimum stiffness of D230 samples, shown in Figure 2.12.

<table>
<thead>
<tr>
<th>Clamp</th>
<th>Stiffness (N/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SC S-T = 10</td>
<td>135</td>
</tr>
<tr>
<td>SC S-T = 6</td>
<td>1154</td>
</tr>
<tr>
<td>3pt (S-T = 6)</td>
<td>1802</td>
</tr>
<tr>
<td>Tension #1 (S-T = 14)</td>
<td>6350</td>
</tr>
<tr>
<td>(0.02% strain)</td>
<td></td>
</tr>
<tr>
<td>Tension #2 (S-T = 14)</td>
<td>6426</td>
</tr>
<tr>
<td>(0.05% strain)</td>
<td></td>
</tr>
</tbody>
</table>

Figure 2.12: D230 samples measured in tension and two thicknesses in SC, along with 3pt. A) as measured and B) tension results shifted to match the $T_g$ of SC results.
Summarizing the results, accurate glassy moduli results can be achieved with any of the three clamps for epoxy and, presumably, similar thermosets provided a span-to-thickness ratio >10 is maintained. The $T_g$ is sensitive to sample dimensions through differences in thermal lags. Above the $T_g$, sample expansion and stiffness must be considered. The three fixed points of DC render the fixture unable to cope with thermal expansion in the sample span direction and yields no useful rubbery data. 3pt and SC fixtures both produce rubbery data that adhere to the theory of rubber elasticity provided the samples are thick enough to maintain appropriate stiffnesses; however, the 3pt values are consistently lower and enough sample sagging is possible that the rubbery modulus measurements cannot be made. SC rubbery data were similar to tension results and should be preferred. These conclusions are summarized in Table 2.7.

<table>
<thead>
<tr>
<th>Clamp</th>
<th>Sample Size Requirements for DMA Properties</th>
<th>Glassy Data</th>
<th>Rubbery Data</th>
</tr>
</thead>
<tbody>
<tr>
<td>3pt</td>
<td>Any but maintain size across samples</td>
<td>S-T &gt; 10</td>
<td>Appears to meet $\nu_{\infty}$ criteria if stiff enough but lower results than SC</td>
</tr>
<tr>
<td>DC</td>
<td>Any but maintain size across samples</td>
<td>S-T &gt; 10</td>
<td>Not suited</td>
</tr>
<tr>
<td>SC</td>
<td>Any but maintain size across samples</td>
<td>S-T &gt; 10</td>
<td>Preferred but samples must be thick enough to ensure stiffness</td>
</tr>
</tbody>
</table>

2.2.4 Discussion

It has been shown that sample dimensions as well as clamp type must be carefully chosen to yield accurate measurements. For many polymeric materials, the best data may be obtained by two samples with different dimensions: a high span-to-thickness ratio
sample for glassy measurements, with a lower S-T ratio sample for rubbery data to ensure adequate stiffness. Many of these suggestions are outlined in the manufacturer’s manual, although the consequences of deviating from the suggestions are not.

A brief literature survey was performed to see what the prevailing practices are regarding clamp and sample dimensions in the greater scientific community. The survey was restricted to published data for thermoset polymers using the 3pt, DC, and SC clamps discussed previously, and gathered on either the TA Instruments Q800 or 2950 DMA, machines with the same operating windows. Of particular interest were the rubbery data and the span-to-thickness ratios. Modulus values were explicitly stated, estimated from plots, or calculated from stated cross-link density values. If multiple values were presented in a paper, only the highest and lowest were compiled. In some circumstances it was difficult to ascertain the basic parameters surrounding the DMA tests; researchers occasionally omitted sample dimensions [36, 50-51, 59], the clamp type used [93-94], the test span [24-26], or appear to report the test span as a sample’s total length [19, 31]. Given a limited number of clamps available, actual sample spans were inferred from stated sample lengths, e.g. a sample described to be a 60 mm DC sample was interpreted to be a 60 mm sample tested in the 35 mm DC clamp. The results are shown in Figure 2.13, Figure 2.14, and Figure 2.15 for 3pt, DC, and SC clamps, respectively, along with the operating limits of the respective clamps.

The 50 mm 3pt clamp was used in the majority of the referenced papers using that clamp type, and as such, meeting the criterion of S-T > 10 for good glassy data is relatively easy. With respect to rubbery modulus data, most of the data were inside the operating window but close to the lower edge. As shown above, 3pt clamps can under-
measure rubbery data, compared to SC and tension clamps. For the DC samples, all are within the operating window; however, none of the rubbery data should be considered valid without closer examination as the constantly decreasing rubbery modulus will not allow for calculation of crosslink density according to rubber elasticity theory [82]. The SC clamp was most common clamp which is fortuitous given the above results; however, most of the reported data has S-T ratios < 10. While most of those with smaller span-to-thickness ratios are comfortably within the operating window suggesting valid rubbery data, those thicker samples likely have artificially lower glassy moduli as per Figure 2.4.

Figure 2.13: Literature values of rubbery modulus data collected using 3pt clamps, grouped by span-to-thickness ratios [11-12, 14-18, 20-22, 95-96].
Figure 2.14: Literature values of rubbery modulus data collected using DC grouped by span-to-thickness ratios [24, 26-32].
Figure 2.15: Literature values of rubbery modulus data collected using SC [37, 39-43, 45-47, 49, 52-58, 60-71, 97-99]. An assumed misplaced decimal point [41] results in shifting the circled points to the left.

2.3 Fracture Toughness

2.3.1 Introduction

Fracture toughness of polymers is an important material property; however the test is extremely sensitive to sample preparation. Each test sample requires a sharp crack to be initiated prior to testing. The sharpness of the crack is rarely defined and several methods of generating the crack exist. ASTM D 5045 [5] specifies that a notch should first be machined into the sample, then a natural crack generated by tapping a razor blade.
The natural crack’s length must be twice the width of the machined notch. If a crack cannot be generated by tapping, alternatively a razor can be slid or sawn across the notch, again with the requirement that the length is twice the width of the machined notch.

In the past researchers have initiated starter cracks by tapping a notch in the sample with a knife blade [100], chilling a razor blade before tapping [101], pressing a razor into the notch [102] and simply drawing a fresh razor blade across the notch [103-104]. The type of razor blade is often not specified, which could be important, considering that single edged razor blades are over twice the thickness of their double-edged counterparts, 0.2 mm vs. 0.1 mm. Also it is rarely clear whether the crack meets the length requirement in the ASTM standard. Ma et al. [105] detail the problems associated with reproducibly creating sufficiently sharp cracks in epoxies and advocated that only “instantly propagated” cracks are sufficiently sharp. They termed cracks to be “instantly propagating” if the crack propagated several millimeters ahead of the razor blade with a single tap of the razor.

Further difficulties arise when measuring fracture toughness of polymers with varying glass transition temperatures or contain filler. If care is not taken to initiate cracks at a constant value of T-T_g, then different sharpness of cracks can be generated, leading to incorrect toughness values. When hard particulate fillers are used there is the possibility that scoring/sawing a crack into the material could simply remove the particulates, resulting in a crack tip with the radius of the particulate.

Thin films of a variety of materials have been used to generate starter cracks. Fluoropolymer films 25 µm thick have been used to generate cracks in end-notched flexural tests for testing mode II fracture in composites [106-107]. Thin metal
spacers also have potential to serve as artificial cracks, though they must be treated with release agent. Zhang and Evans used 50 µm stainless steel foil that had been coated with release agent to investigate the toughness of various epoxies at cryogenic and room temperatures [108]. They determined that a 50 µm was a sufficiently fine starting notch and noted that using a 300 µm notch led to much high initial loads and a work of fracture three times that given by the thinner foil. At cryogenic temperatures, with the 50 µm notch, low works of fracture were reported for all resins with the work of fracture generally increasing with increasing temperature. At room temperature ductile fracture was reported for some resins. Oddly, in one case, a higher work of fracture was reported at 77 K than at 300 K. The work of fracture is related, but not necessarily identical to $G_{1c}$.

Research showed that films can be used to start cracks in certain situations, with the most success at cryogenic temperatures; however, 50 µm films are still thick relative to a razor blade. In addition little work has been done at ambient temperature or with toughened epoxies. None of the work has compared film-initiated fracture with other types of sharp cracks. The goal of this work is to compare crack initiation methods in single edge notch bend (SENB) fracture toughness measurements for the purpose of finding the most suitable method for yielding consistently sharp cracks regardless of the $T-T_g$ relationship at crack initiation. The approach involves inserting several types of films (fluoropolymers, stainless steel, and aluminum) as crack initiators into the SENB specimens during cure and comparing those results to more traditional crack initiation methods, such as the instantly propagating and razor scoring techniques. The various crack initiation methods are evaluated for several epoxy systems, including unmodified,
rubber toughened, and hard particle-toughened to elucidate any contributions of resin $T_g$ or toughness on the measured fracture toughness values.

### 2.3.2 Experimental

Fluoropolymer films with thicknesses of 12.7, 25.4 and 50.8 µm (0.5, 1, and 2 mil) were obtained from CS Hyde Co. (Lake Villa, IL). Aluminum foil (Al) with a thickness of 18 µm (0.7 mil) was obtained from Thermo Fisher Scientific Inc. (Pittsburgh, PA). Stainless steel (SS) feeler gauges also with thicknesses of 12.7, 25.4 and 50.8 µm were obtained from McMaster-Carr. The polymer and Al films were cut to appropriate widths (~ 12.7 mm) while the SS was used as received. Both the Al and SS were coated with a release agent (Frekote 55-NC, Henkel Corp) before use.

Four resins are used in this work, two with similar lower $T_g$s and two with similar higher $T_g$s. One resin of each set is rubber toughened. Two-part rubber toughened epoxies, SC-15 and SC-79, were obtained from Applied Poleramic (Benicia, CA). The non-toughened epoxies both contained high purity diglycidyl ether of bisphenol A (DGEBA) (Epon 825, Momentive Specialty Chemicals, Houston TX, Figure 2.3A) cured with a stoichiometric amount of PACM or Jeffamine D-230, Figure 2.3B and E respectively. In addition, 10 vol% 1 µm silica (Fiber Optic Center, Inc.) is added to the 825-D230 sample to create a hard particle-toughened resin.

The resins were well mixed using an ARE 250 Thinky centrifugal mixer (Thinky Corp, Japan) and then degassed under vacuum until the foam collapsed. For the 825-D230 samples with silica, the silica was first sonicated with the D230 in a bath sonicator. The epoxy was then hand mixed into the silica/D230 mixture, with no degassing. After
mixing the resins were then poured into the preheated aluminum mold, described below, and cured as described in Table 2.8. All samples were removed from the mold before post curing; the film/foil remained in the sample.

Table 2.8: Formulations and cure schedule of resins.

<table>
<thead>
<tr>
<th>Resin</th>
<th>Mix Ratio (by weight)</th>
<th>Cure Schedule (mold preheated to 60°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SC-15</td>
<td>100/30</td>
<td>4 h at 60 °C + 3 h at 121 °C</td>
</tr>
<tr>
<td>SC-79</td>
<td>100/40</td>
<td>4 h at 60 °C + 1 h at 177 °C</td>
</tr>
<tr>
<td>825-D230</td>
<td>100/34</td>
<td>gel at 60 °C + 2 h at 80 °C + 2 h at 125 °C</td>
</tr>
<tr>
<td>825-PACM</td>
<td>100/30</td>
<td>2 h at 60 °C + 2 h at 80 °C + 2 h at 160 °C</td>
</tr>
</tbody>
</table>

Sample blocks, approximately 12.7 mm x 76 mm x 102 mm, were made in an aluminum mold that had been coated with release agent. The top portion of the mold was made of two portions such that the foil could be cured in the samples at the correct depth, as shown in Figure 2.16A; rubber gaskets helped seal the seam between the film/foil and the mold’s top pieces. Samples with approximate dimensions of 6 mm x 12.7 m x 76 mm were then cut from the block, resulting in SENB specimens, as shown in Figure 2.16B, with the foil extending approximately 6 mm into the samples. For comparison samples of the resins were made in the same mold, except with a nominal thickness of 19 mm. Those resin blocks were cut into sections ~ 9.5 mm x 19 mm x 102 mm and “instantly propagated” [105] cracks were made in the samples by tapping a single edged razor blade into a machined notch. The 825-PACM, SC-15, and SC-79 samples were cracked at room temperature while the 825-D230, filled and unfilled, samples were cracked after chilling both the samples and razor blades to approximately -20 °C. Additionally, cracks were initiated by scoring a machined notch with a double-edged razor blade. Fracture
toughness of the samples was measured according to ASTM D 5045-99 with the exception of the initial crack generation method. Testing was done at room temperature on an Instron screw-driven testing frame using a 5 kN load cell and crosshead speed of 10 mm/min.

Figure 2.16: A) Sketch of mold that holds PTFE film or metal foils in place while the resin cures and B) slice of the resin block with a thin crack.

### 2.3.3 Results and Discussion

In order to ensure the film-cracked toughness measurements had the potential to approach those of instantly propagated cracks, the films must first be reproducibly embedded in the resin. The effectiveness of film inserts as crack initiators relied heavily on the ability to maintain a straight crack during resin cure. Processing a suitable crack was influenced by film material type and its thickness. The processing characteristics of the different film materials are discussed below, followed by a discussion of the toughness measurements.
2.3.3.1 Sample Fabrication

For the fluoropolymers, it proved to be difficult for the film to remain taut during cure due to either slippage between the film and the mold/gasket or because the fluoropolymer had a much higher coefficient of thermal expansion compared to the aluminum mold. When tension was lost before resin gelation, the film curved in either the x-y plane or the z (depth) direction. Curvature in the x-y plane simply resulted in a wandering center-point, whereas curvature in the z direction yielded a film that is not perpendicular to the bottom, shown in Figure 2.17, and in extreme cases appears more similar to a “J”. This occurred more easily in the thinner films, as attempts to apply tension produced stretching and breaking of the film. As a consequence, no samples suitable for testing were made using the 12.7 µm fluoropolymer film and only one set each was made with the 25.4 µm PTFE film for the SC-15 and SC-79. Multiple attempts were made using the 50.8 µm PTFE film with those resins, the results of the best and worst sets will be discussed. No sample sets were made using fluoropolymers with the other resins due to the above mentioned difficulties.

![Figure 2.17: 50.8 µm PTFE embedded in SC-15 exhibiting moderate curling.](image)

Al is much stiffer than the fluoropolymer films and curvature in the z direction was limited; however, some curvature in the x-y direction still occurred. Excessive
tension caused the foil to tear and the foil also easily wrinkled; care was taken to
minimize wrinkles while cutting the foil to size. Al foil initiated sample sets were made
for the SC-15, SC-79 and the unfilled 825-D230.

The SS was the stiffest and easiest to work with, even at the 12.7 µm thickness.
Tension was easy to maintain and there was no stretching. Samples of all resins, except
SC-79, were made using each of the three SS thicknesses.

2.3.3.2 Fracture Toughness Results & Discussion

The fracture toughness ($K_{1c}$ and $G_{1c}$) results for the resins are shown in Table 2.9
along with the $T_g$s, as determined by DMA. Normalized toughness for the SC-15 and
SC-79 samples with PTFE initiated cracks are shown in Figure 2.18, along with those
initiated by scoring. Figure 2.19 shows the results with cracks initiated by various
thicknesses of SS, as well as by Al foil and scoring. In all cases the lowest values were
those obtained from the “instantly propagated” cracks made by tapping a razor blade until
the crack grew; those results were used to normalize the others. The samples with
instantly propagated cracks also had the lowest standard deviations. No other method
had consistently low standard deviations. In some cases, such as D230 with Al initiated
cracks, the standard deviations could be as much as four time (for $K_{1c}$) or ten times (for
$G_{1c}$) greater than those with instantly propagated cracks. $G_{1c}$ can be calculated either
from $K_{1c}$ using the modulus and Poisson’s ratio or from the area under the load-
displacement curve. The results in Table 2.9, Figure 2.18, and Figure 2.19 are from
results of the area under the curve; values calculated from $K_{1c}$ are very similar.
Table 2.9: Fracture toughness measured with instantly propagated cracks and $T_g$ of resins.

<table>
<thead>
<tr>
<th>Resin</th>
<th>$K_{1c}$ (MPa m$^{1/2}$)</th>
<th>$G_{1c}$ (J/m$^2$)</th>
<th>$T_g$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SC-15</td>
<td>1.49 ± 0.02</td>
<td>810 ± 30</td>
<td>96 ± 2</td>
</tr>
<tr>
<td>SC-79</td>
<td>0.69 ± 0.03</td>
<td>130 ± 10</td>
<td>160 ± 4</td>
</tr>
<tr>
<td>825-PACM</td>
<td>0.86 ± 0.07</td>
<td>270 ± 30</td>
<td>171 ± 1</td>
</tr>
<tr>
<td>825-D230</td>
<td>0.86 ± 0.09</td>
<td>210 ± 50</td>
<td>93 ± 1</td>
</tr>
<tr>
<td>825-D230 + 10 vol% silica</td>
<td>1.18 ± 0.04</td>
<td>350 ± 60</td>
<td>94 ± 1</td>
</tr>
</tbody>
</table>

In general there is a lot of variation in the samples with PTFE initiated cracks. For the same thickness of PTFE in SC-15 one set of samples showed an apparent $K_{1c}$ increase of 20%, while another set showed 60% increase compared to the samples with instantly propagated cracks. Similarly for SC-79, one set showed an increase of 20% while another showed 100%, illustrating poor reproducibility using fluoropolymer films. $G_{1c}$ and $K_{1c}$ follow the same trends although the differences are accentuated in $G_{1c}$. 
Figure 2.18: Normalized toughness values for SC-15 and SC-79, with PTFE initiated cracks: A) normalized $G_{1c}$ and B) normalized $K_{1c}$.
Figure 2.19: Normalized toughness values for resins with various types of initiated cracks: A) normalized $G_{1c}$ and B) normalized $K_{1c}$.
For SC-15 and 825-D230, the Al foil provided the best film results and was better than razor scoring, despite being thicker than the 12.7 µm SS; also it was very similar to the scored samples in SC-79. This is a result of the end profile of the material as the crack tip radius is a critical parameter in fracture toughness measurements [109]. Figure 2.20 shows the tip of the crack formed by the Al in SC-15. Most of the crack is 18 µm in width, as specified by the manufacturer, but near the tip, the width decreases to a point approximately 3 µm in radius, presumably an effect of cutting and smoothing any wrinkles from the foil. In contrast is the SS, as shown in Figure 2.21. The 50.8 µm SS (Figure 2.21) very clearly shows a squared-off profile, with the thinner SS also being less pointed than the Al foil. The instantly propagated cracks are much sharper, as shown in Figure 2.22, for D230, with a tip radius of < 1 µm.

This effect of crack tip radius has been studied before. A recent study controlled the crack tip radius in an epoxy using a variety of techniques including: instantly propagated cracks, femtosecond pulsed laser ablation, and scoring with specially designed razors with different tip radii [110]. Their instantly propagated cracks had radii of under 0.2 µm while the best razor scored samples had radii of 5 µm. This increased tip radius resulted in more than doubling the apparent toughness.

Kinloch and Williams did not directly alter the crack tip radius, but observed and modeled similar behavior by controlling initial crack blunting by varying the polymer yield stress [111]. As the yield stress decreases, the initial crack blunted more easily. An effect of a blunter crack tip is a lowering of the stress concentration effect which requires higher applied stress to cause fracture, resulting in higher apparent toughness.
Figure 2.20: Tip profile of Al foil in SC-15.

Figure 2.21: Tip profile of 50.8 µm SS in SC-15.
While the yield stresses and exact tip profiles were not measured here, some conclusions can be drawn from Figure 2.18 and Figure 2.19. In all cases of film-initiated cracks, the 825-D230 resin has the greatest increases in apparent toughness and is very sensitive to the starter crack type. In the best case, with Al, the measured $K_{1c}$ is almost twice that measured with an instantly propagated crack. Therefore, it can be inferred that 825-D230 has the lowest yield stress of the resins tested. The addition of silica particles limits this effect somewhat, possibly by slightly blunting instantly propagated cracks. The other resins all have similar increases when the cracks are film-initiated, despite only some being rubber toughened. For the rubber-toughened resins, the toughening rubber purposefully blunts the crack, so even an instantly propagated crack may not be a sharp as in a non-toughened resin. hence starting with a blunter crack is not as important. In PACM’s case, its compressive yield strength has been reported to be 120 MPa [77]. For resins with similar yield strengths, Kinloch and Williams saw limited signs of crack blunting so $K_{1c}$ is less dependent on the crack tip radius [111].

Despite the artificially high toughness values, most fracture surfaces are predominately glassy and smooth. Some of the higher toughness samples (i.e. 825-D230 with 50.8 µm SS) showed some plastic deformation near the crack initiation but the majority of the fracture surfaces are smooth. Also the high apparent toughness samples had sufficient excess energy when the samples broke that the fragments flew apart, whereas the samples with instantly propagated cracks had less residual energy and the pieces moved less.
2.4 Conclusions

Five epoxy networks were characterized by DMA using three different clamps and different span-to-thickness ratios. Provided the span-to-thickness ratio was 11, the glassy room temperature modulus matched that as measured according to ASTM D 790 for all three clamps. In the rubbery region thermal expansion and sample stiffness must be considered. Samples with span-to-thickness ratios > 10 resulted in sample stiffnesses that were outside the sensitivity limits of the machine. High expansion materials cannot be accurately tested on DC clamps due to the three fixed points. 3pt can handle expansion better but the sample can experience sagging at higher temperatures. SC, with some lateral clamp movement, was best suited for characterizing rubbery moduli, although a thicker sample than would be tested for glassy measurements is required to
maintain adequate stiffness. While only epoxy-amine networks were tested, these findings are likely applicable to other thermoset polymers as well.

A brief literature survey showed that many researchers are unaware of the manufacturer’s recommendations and the importance of sample dimensions. Published results include span-to-thickness ratios < 10, resulting in inaccurate glassy modulus measurements, and rubbery data outside the sensitivity limits of the instruments. For most unfilled thermoset polymers, we concur with the manufacturer’s recommendation of using the SC clamp with a span-to-thickness ratio of > 10 for glassy measurements and a smaller ratio as necessary to stay within the operating window for rubbery modulus measurements.

With regards to fracture toughness, while the SS or other films cannot reproduce the true $K_{IC}$ values, they can generate values similar to those generated by scored or non-propagated cracks and thus could be a valid method for initiating cracks for relative toughness measurements in situations where “instantly propagated” cracks are difficult or impossible to generate. However, care must be taken to ensure that the tip profile of the foil/film is constant across samples.
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Chapter 3: Epoxies Cured with Blends of Polyetheramines

3.1 Introduction

As mentioned in Chapter 1, one Aim of this research is to investigate bimodal distributions in epoxy-amine networks and determine whether those distributions are an avenue to increase fracture toughness. Bimodal distributions have shown promise in increasing fracture properties. In vinyl esters the toughness was improved by using a bimodal blend of vinyl esters instead of a single molecular weight distribution [1]. Certain bimodal blends of epoxies cured with a single amine have also led to increased toughness, though the different molecular weight epoxies led to phase separation [2]. Other work with bimodal epoxy blends resulted in no change in properties compared to monodisperse epoxies, though both the epoxy and amine contained similar phenol-based structures [3]. Instead of simply controlling the cross-link density, here DGEBA is cured with bimodal blends of structurally different polyetheramines with no phase separation. These blends will be compared to those of resins made with a single amine distribution.

3.2 Experimental

3.2.1 Blend Formulation

Epon 825 (Hexion Specialty Chem.), Figure 3.1A, is a high purity diglycidyl ether of bisphenol A (DGEBA), with an epoxide equivalent weight of 175-176 g/mol. The amines used are Jeffamine® diamines (Huntsman) which are polyetheramines with the structure as shown in Figure 3.1B. Three Jeffamines were used: D230, D400, and
D2000, where \( n \) is approximately 2.6, 6.1 and 33, respectively and have approximate molecular weights of 240 g/mol, 445 g/mol, and 1980 g/mol.

\[
\begin{align*}
\text{A) } & \quad \begin{array}{c}
\begin{array}{c}
\text{O} \quad \text{O} \quad \text{O} \quad \text{O}
\end{array}
\end{array} \\
\text{B) } & \quad \begin{array}{c}
\text{H}_2\text{N} \quad \text{O} \quad \text{NH}_2
\end{array}
\end{align*}
\]

Figure 3.1: Structure of A) Epon 825 (DGEBA) and B) Jeffamine polyetheramines, \( n \) is \( \sim 2.8, 6.4, \) and 33 for D230, D400, and D2000 respectively.

Several bimodal blends were considered. The first matched the amine hydrogen equivalent weight (AHEW) of D400 using a mixture of D230 and D2000. Matching the AHEW matches the molar average weight of the amine. Similar blends were made using D230/D2000 and D400/D2000 to match a theoretical amine with molecular weight of 1000 g/mol. Table 3.1 summarizes the blends and typical proportions of each component. The AHEW for the Jeffamines were obtained from the manufacturer’s certificates of analysis and slight batch-to-batch variations were observed and accounted for in the formulations. The AHEW for D230 ranged from 59.1-61.0, D400’s was 111.1, while D2000’s was either 495 or 500. In all cases, a stoichiometric amount of epoxy and amine were used, with two epoxide groups per amine.
Table 3.1: Amounts of Amine per 100g Epon 825. A prefix of D# signifies a resin made using a single amine of weight # while B# signifies a bimodal blend with an average amine weight of #. The lower molecular weight component of the blend is indicated in parentheses.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>D230</td>
<td>34.3</td>
<td>0</td>
<td>0</td>
<td>34.3</td>
<td>240</td>
</tr>
<tr>
<td>D400</td>
<td>0</td>
<td>63.1</td>
<td>0</td>
<td>63.1</td>
<td>445</td>
</tr>
<tr>
<td>D2000</td>
<td>0</td>
<td>0</td>
<td>281.3</td>
<td>281.3</td>
<td>1980</td>
</tr>
<tr>
<td>B270 (D230)</td>
<td>33.8</td>
<td>0</td>
<td>4.6</td>
<td>38.4</td>
<td>270</td>
</tr>
<tr>
<td>B390 (D230)</td>
<td>31.4</td>
<td>0</td>
<td>24.3</td>
<td>55.7</td>
<td>390</td>
</tr>
<tr>
<td>B440 (D230)</td>
<td>30.3</td>
<td>0</td>
<td>32.8</td>
<td>63.1</td>
<td>440</td>
</tr>
<tr>
<td>B620 (D400)</td>
<td>0</td>
<td>56.0</td>
<td>31.7</td>
<td>87.7</td>
<td>620</td>
</tr>
<tr>
<td>B1000 (D230)</td>
<td>19.3</td>
<td>0</td>
<td>122.7</td>
<td>142.0</td>
<td>1000</td>
</tr>
<tr>
<td>B1000 (D400)</td>
<td>0</td>
<td>40.3</td>
<td>101.7</td>
<td>142.0</td>
<td>1000</td>
</tr>
</tbody>
</table>

3.2.2 Resin Cure

The Epon 825 was warmed to 45–50 °C and degassed under vacuum to melt any crystallized material and to remove any volatiles. The appropriate masses of the Jeffamines were then added to the epoxies and were thoroughly mixed using an ARE 250 Thinky centrifugal mixer. The mixed resins were then degassed under vacuum just long enough for any trapped air to foam and collapse, for generally fewer than five minutes. The resin was then poured into molds, silicon rubber or aluminum, and cured for two hours at 80 °C. The samples were then removed from the mold and post cured for two hours at 125 °C. Mixtures of Epon 825 and Jeffamine D2000 reacted more slowly than other formulations and were not gelled after two hours at 80 °C; those samples were instead cured at 125 °C for four hours. All cured samples were transparent indicating that phase separation did not occur.
3.2.3 Extent of Cure

The extent of cure for all samples was tested in a TA Instruments Q1000 DSC. 5–10 mg of freshly prepared sample was sealed in hermetic aluminum DSC pans and tested according to the desired cure and post cure schedule described above. After the cure, the sample was quickly cooled to 0 °C to quench the reaction, and then ramped at 5 °C/minute to 300 °C to observe any residual cure. The total heat of cure was determined by taking 5–10 mg of uncured resins and increasing the temperature at 5 °C/minute from room temperature to 300 °C. Under these conditions, the exothermic peak of the D2000 samples did not return to the baseline due to slower reaction; instead D2000 samples were ramped at 3 °C/minute to ensure there was a baseline for peak integration. The exothermic peak was integrated using TA Universal Analysis software; an average of at least three runs was used. For the full cure cycle samples, only the final ramp was examined for signs of an exothermic peak, signifying a residual heat of reaction.

Near-infrared (NIR) spectroscopy was also used to investigate the extent of cure. In the NIR region, epoxide groups show peaks at 4530 and 6060 cm\(^{-1}\); primary amines have a peak at 4925 cm\(^{-1}\) while a peak at 6534 cm\(^{-1}\) is caused by primary and secondary amines [4]. Spectra of the neat monomers and the cured samples were taken using a Nicolet Nexus 870 infrared spectrometer. The spectra of the cured samples were qualitatively examined for residual epoxy or amine functionality.

3.2.4 Reaction Kinetics

In addition to simply qualitative extent of cure analysis, the cure kinetics are also followed using FTIR. Epoxy-amine reactions have been widely studied using near-
infrared (NIR) spectroscopy [5-7]. Mid-IR (MIR) has also been used to follow epoxy-amine reactions; however, it has been shown that MIR can underreport the actual consumption of epoxy groups [8]. In the MIR region the 915 cm$^{-1}$ peak is commonly assigned to the epoxy peak; however it is not truly unique to the epoxy group [9]. Epoxy peaks appear in two locations in the NIR region, at 6060 and 4530 cm$^{-1}$. The 6060 cm$^{-1}$ peak overlaps with the aromatic peak at 5960 cm$^{-1}$, so must be self-deconvoluted for quantitative analysis [4-5, 7] whereas the 4530 cm$^{-1}$ peak can be used to directly monitor epoxy concentrations [7-8]. The primary amine peak appears around 4925 cm$^{-1}$ and a combination of the primary and secondary amines appears as a broad peak around 6930 cm$^{-1}$. Absent any undesired reactions (epoxy homopolymerization [4], hydroxyl-epoxy etherification [5]) the mass balance of the measured epoxy and amine concentrations can be given as in equations 3.1 and 3.2:

$$[EP]_0 = [EP] + [SA] + 2[TA]$$  

$$[PA]_0 = [PA] + [SA] + [TA]$$

where $[EP]_0$ and $[PA]_0$ are the initial epoxy and primary amine concentrations, respectively and $[EP]$, $[PA]$, $[SA]$, and $[TA]$ are the epoxy, primary amine, secondary amine, and tertiary amine concentrations at time $t$. Experimental concentrations of epoxy and primary amine are calculated from the FTIR data while the corresponding secondary and tertiary amine concentrations can be calculated from the mass balance as shown in 3.3 and 3.4, respectively.

$$[SA] = 2([PA]_0 - [PA]) - ([EP]_0 - [EP])$$
\[ [TA] = ([EP]_0 - [EP]) - ([PA]_0 - [PA]) \] 3.4

As mentioned in Chapter 1, the epoxy-amine reaction is catalyzed by hydroxyl groups and as one hydroxyl is formed for every epoxy-amine reaction, the reaction becomes autocatalytic; tracking the hydroxyl concentrations is important. The concentration of hydroxyls at time \( t \), \([OH]_t\), is given by equation 3.5.

\[ [OH] = [OH]_{auto} + [OH]_0 \] 3.5

where \( [OH]_{auto} \) is the concentration of hydroxyls formed by the epoxy-amine reaction and \( [OH]_0 \) is the initial concentration. \( [OH]_{auto} \) can be determined by the concentrations of the secondary and tertiary amines, equation 3.6:

\[ [OH]_{auto} = [SA] + 2[TA] \] 3.6

The initial hydroxyl concentration is predominately determined by the \( n \) value of the DGEBA epoxy monomer; however some may be present from the polyetheramines. The Jeffamines are made from polyether glycols [10] and residual hydroxyls may be present. For example, the specification sheet for D2000 reports 93% amine conversion. D400 has at least 98% amine conversion, while it is not specified for D230. Other sources of initial hydroxyls include impurities such as water; however, they are assumed to be minimal. For 825-D2000, in Epon 825 \( n \approx 0.04 \), and D2000 has 93% amine conversion so \( [OH]_0 \) is given by equation 3.7.

\[ [OH]_0 = 0.04\frac{[EP]_0}{2} + \left( \frac{[PA]_0}{0.93} - [PA]_0 \right) = 0.04\frac{[EP]_0}{2} + 0.075 \cdot [PA]_0 \] 3.7

While the 7% not converted to amines may not all be hydroxyls, in the case of 825-D2000, the concentration is high enough that it cannot be ignored, for the other
resins the residual Jeffamine hydroxyls are considered negligible and the second term reduces to zero.

Epoxy-amine reactions can proceed through a non-catalytic, equations 3.8 and 3.9, or an autocatalytic pathway, equations 3.10 and 3.11.

\[ [PA] + [EP] \xrightarrow{k_{i}} [SA] + [OH] \]
\[ [SA] + [EP] \xrightarrow{k_{i}} [TA] + [OH] \]
\[ [PA] + [EP] + [OH] \xrightarrow{k_{i}} [SA] + 2[OH] \]
\[ [SA] + [EP] + [OH] \xrightarrow{k_{i}} [TA] + 2[OH] \]

In model systems the non-catalytic pathway is often considered; however, here the hydroxyls present initially allow us to focus solely on the autocatalytic pathway. Combining equations 3.6 and 3.8-3.11 the rate expressions for the epoxy, primary, secondary and tertiary amines: equations 3.12-3.15, respectively.

\[ \frac{d[EP]}{dt} = -k_1[PA][EP][OH]_{auto} + [OH]_0 - k_2[EP][SA][OH]_{auto} + [OH]_0 \]
\[ \frac{d[PA]}{dt} = -k_1[PA][EP][OH]_{auto} + [OH]_0 \]
\[
\frac{d[SA]}{dt} = k_1 [PA][EP][OH]_{auto} + [OH]_0 - k_2 [EP][SA][OH]_{auto} + [OH]_0 
\]
3.14

\[
\frac{d[TA]}{dt} = k_2 [EP][SA][OH]_{auto} + [OH]_0 
\]
3.15

Equations 3.12 - 3.15 were solved using a MATLAB non-linear ODE solver with initial concentrations. Epoxy and amine concentrations for different values of \(k_1\) and \(k_2\) were calculated as was the deviation between the calculated and experimental. The best fit values of \(k_1\) and \(k_2\) were those that minimized the deviation between the experimental and calculated concentrations of epoxy and primary amine.

### 3.2.4.1 FTIR Setup

A Nexus 870 FTIR (Thermo-Nicolet Corp) was used to record the NIR spectra of the resin samples at regular intervals as they cured at 80 °C. Each spectrum is the average of 8 scans recorded at 8 cm\(^{-1}\) resolution. The low resolution and number of scans were chosen to minimize the collection time per point; each spectrum is collected in 4.2 s; more scans, such as 32 scans at 8 cm\(^{-1}\) resolution as used elsewhere [7], require 16.8 s. Sample holders consisted of a 2 mm thick nitrile gasket sandwiched between two glass circles, approximately 16 mm diameter and 1 mm thick, resulting in a 2mm x 10mm cylindrical sample space, with the IR beam perpendicular to the smaller dimension. 825/D230 was used as a sealant to secure the gasket to the glass and prevent leakage. 825/D230 was chosen as a sealant to prevent unknown species from commercial adhesives from leaching into the sample and contaminating the spectrum during testing. A temperature controller maintained an aluminum block at 80 °C (±0.5 °C). The sample
holder fit in the center of the aluminum block, allowing circumferential heating, as shown in Figure 3.2.

Figure 3.2: Schematic of temperature controlled FTIR sample holder.

The empty sample holder was inserted into the aluminum block and a background scan was taken after thermal equilibration. The warm sample holder was removed from the block, filled with freshly mixed resin and reinserted, at which point data collection began. Scans were taken every 90 s for most samples, except for samples of 825/D2000 where the interval was increased to every 120 s. For most samples, the temperature was increased to 125 °C after two hours, mimicking the cure cycle used for DMA and fracture toughness samples. This post cure was used to assess the extent of cure; kinetic parameters are only calculated in the pre-gelation stage, which in most cases occurred within two hours at 80 °C. Again 825/D2000 is the exception. For other samples it is
cured at 125 °C for four hours, but for the purpose of determining its kinetic rate constants, it is cured at the same temperature as the others but for 12 hours.

### 3.2.5 Polymer Characterization

#### 3.2.5.1 DMA

Samples with approximate dimensions of $35 \times 12 \times 3.25 \text{ mm}^3$ were tested on a TA Instruments Q800 Dynamic Mechanical Analyzer using the single cantilever clamp, operating at 1 Hz with 7.5 μm displacement. Due to its low modulus above $T_g$, the 825/D2000 samples required thicker samples (5–5.5 mm) to yield valid results in the rubbery region; however, since altering the aspect ratio of samples can affect the modulus, only rubbery modulus data was used from the thicker samples [11]. These experiments were performed before the DMA analysis detailed in Chapter 2, so the recommended span-to-thickness ratio $>10$ was not used for glassy modulus measurements; however, the span-to-thickness ratios were similar for glassy moduli and all samples were thick enough to yield good rubbery modulus data. To compare samples with a similar thermal history, samples of each resin were cooled to -100 °C then allowed 60 minutes to reach equilibrium before increasing the temperature by 2 °C/minute to 160 °C. The clamps were tightened after approximately 30 minutes at -100 °C.

The temperature at which the peak in the loss modulus occurred was considered the glass transition temperature of the resin [12]. All samples had a definite point in the loss modulus where the rubbery modulus began to increase with increasing temperature; this point was used to calculate the molecular weight between cross-links, $M_c$. The theory of rubber elasticity was used to calculate the $M_c$, equation 3.16, from DMA data:
\[ M_c = \frac{3RT\rho}{E'} \]  

where \( R \) is the gas constant, \( T \) the absolute temperature, \( \rho \) the density, and \( E' \) the modulus of the rubbery plateau. Rubber elasticity applies to polymers with low cross-link densities and may not give completely accurate cross-link density measurements for highly cross-linked epoxies [13]. Nonetheless, numerous researchers have used it as a measure of cross-link density and it seems to show good trends for sample sets with similar chemistries [14-15].

### 3.2.5.1.1 Time-Temperature Superposition

Another set of samples were tested across multiple frequencies in order to perform time-temperature superposition (TTS). TTS relies on time-temperature equivalence: the assumption that changes in temperature are equivalent to those seen by changes in frequency [11]. This allows DMA isothermal frequency sweeps to be used to extend the testing frequency outside the normal range – to time spans that are either too short or too long to be reasonably measured. In addition parameters characterizing the viscoelastic relaxations can be determined. This method is referred to as a method of reduced variables in that multiplexed modulus versus frequency and temperature data is reduced to modulus versus frequency by shifting the data horizontally relative to a reference curve to create a “master” curve [16]. For example, in Figure 3.3A and B, the storage and loss moduli data are shifted right or left, with a slight vertical correction relative to a reference to create the master curves in Figure 3.3C and D. Superposition can also be achieved with other variables such as stress [17-18], strain [19], and aging time [20].
Figure 3.3: Multiple temperatures of A) storage and B) loss modulus versus frequency and shifted or reduced C) storage and D) loss modulus versus reduced frequency. 93 °C is the reference temperature.

The reduced modulus (storage or loss) is expressed as:
\[ E_{\text{reduced}} = \frac{E T_0 \rho_0}{T \rho} \]  

(3.17)

with \( T_0 \) being the reference temperature, \( T \) the test temperature, both in Kelvin, and \( \rho \) the density. In this work the temperature specific densities are used, as discussed in section 3.2.5.2, and when unavailable, the ratio of \( \frac{\rho_0}{\rho} \) is taken to be unity. At short times or high frequencies, i.e. in the glassy region, the \( \frac{T_0}{T} \) factor from eq. 3.17 is not applicable as the relaxation times are too long relative to the measuring frequency [16]. The reduced modulus is plotted versus the reduced frequency, eq. 3.18:

\[ Freq_{\text{reduced}} = f \cdot a_T \]  

(3.18)

where \( f \) is the frequency and \( a_T \) is the shift factor, thus generating the master curves as illustrated in Figure 3.3C and D.

The Williams-Landel-Ferry (WLF) expression [21] relates the shift factors and their temperatures and describes the temperature dependence of the distribution of relaxation times, equation 3.19:

\[ \log a_T = \frac{-c_1^0(T - T_0)}{c_2^0 + T - T_0} \]  

(3.19)

where \( c_1^0 \) is a dimensionless material constant, \( c_2^0 \) is a material constant with units of temperature, usually °C, while \( T \) and \( T_0 \) are the temperature and reference temperature. An activation energy, \( \Delta H_a \), for the main viscoelastic relaxation can be calculated from the material constants \( c_1^0 \) and \( c_2^0 \) and the \( T_g \), assuming the \( T_g \) is the reference temperature, equation 3.20:
\[ \Delta H_a = \frac{2.303 R c_1^0 c_2^0 T_g^2}{(c_2^0)^2} \]  

3.20

One limitation of the WLF method is that it is limited to the glass transition temperature; no information on secondary transitions is obtained. An alternative expression for \( \Delta H_a \) that can be applied to secondary transitions is derived from the relaxation shifts along the temperature axis to varying extents as a function of frequency due to differing Arrhenius activation energies:

\[ \Delta H_a = -R \frac{d \ln f}{d \left( \frac{1}{T} \right)} \]  

3.21

where \( R \) is the universal gas constant, and \( T \) is the temperature of the relaxation (\( T_g \), \( T_\beta \), or peak of tan \( \delta \)) of interest at the corresponding frequency in Kelvin.

Samples were tested using the DC geometry using step-wise isothermal frequency sweeps. Temperature steps were 5 °C increments away from the \( T_g \) and 3 °C close to the \( T_g \), with 5 minutes of isothermal time for the samples to reach equilibrium. Each frequency sweep contained frequencies of 0.1, 0.22, 0.46, 1, 2.2, 4.6, 10, 21.5, and 30 Hz. Higher \( T_g \) samples, i.e. D230 through B440 samples, were tested from 0 °C to 150 °C, while ambient and sub-ambient \( T_g \) samples started at -20°C (B620), -75° (both B1000s) or -100°C (D2000). The reference temperature was either the \( T_g \), using the peak of the loss modulus from the typical 1 Hz and 2 °C/min DMA runs as the \( T_g \), or the closest isothermal step to that value. Given the length of time required per run, up to 30 hours per sample, often only a single sample per formulation was tested in this manner.

Additional tests were performed using the single cantilever clamp with the sample thickness ~1.7 mm as determined to be optimal for storage modulus measurements in
Chapter 2. The main purpose of these additional tests was to investigate the beta and any other secondary transitions, as will be described later; however, the data were also analyzed by the WLF method. Additionally, thicker, ~3 mm, samples of D230 and D400 were also tested on the SC clamp, ensuring valid rubbery data. Samples for all resins except for the D230, D2000 and the B1000 blends, were cooled to -100°C and allowed to equilibrate for 30 minutes. The temperature was increased, stepwise, in 2 °C increments to 150 °C; for each step, a five minute isothermal step was allowed for thermal equilibration before the frequency sweep. To reduce time and liquid nitrogen required, the measured frequencies were changed to 0.1, 0.5, 1, 5, 10, 30, and 50 Hz; fewer frequencies below 1 Hz greatly reduced the measurement time. The D230 samples were tested using the frequencies and temperature steps stated previously for the DC samples and the D2000 sample was cooled to -140°C but otherwise tested as described above. The B1000 blends were not tested in this manner as the DC DMA runs for those samples started at -75 °C and any sign of beta transitions was obscured by the main transition.

3.2.5.2 Density and CTE

The densities of all samples were measured using the water displacement method outlined in ASTM Standard D792–00 [22]. Thermal expansion data in both the rubbery and glassy regions were measured using a TA Instruments Q400 Thermomechanical analyzer. The coefficients of thermal expansion, CTE, were calculated by equation 3.22:

\[
\alpha = \frac{1}{l_0} \frac{\Delta l}{\Delta T}
\]

where \( l_0 \) is the original length, \( \Delta l \) the change in length, and \( \Delta T \) the change in temperature. Samples were made, following the cure procedures described above, in aluminum molds
measuring 10 x 10 x 55 mm$^3$. The molds were not completely filled, yielding samples approximately 6 x 10 x 55 mm$^3$. From these bars, smaller samples with nominal dimensions of 6 x 6 x 10 mm$^3$ were cut. Samples were tested in the unaltered 10 mm direction and three to five samples per formulation were tested. A constant force of 0.05 N was used for both the preload and the applied load. Samples were heated from room temperature to 125 °C, cooled to -70 °C, then heated to 150 °C at 3 °C/min. The initial heating cycle was to remove any residual stress. The CTE values from the final cycle, from -70 to 150 °C were used to calculate the density as a function of temperature assuming isotropic behavior, equation 3.23:

$$\rho(T) = \frac{\rho_0}{(1 + \Delta)^3}$$  \hspace{1cm} 3.23

where $\Delta = CTE \times (T - T_0)$ in the same units of length as used in $\rho_0$.

### 3.2.5.3 Fracture Toughness

Fracture toughness was measured on samples having $T_g$s above 40 °C using the compact tension geometry and according to ASTM D5045 [23]. Samples were cured in silicon rubber molds with nominal dimensions of 30.5 x 32 x 12.7 mm$^3$. A 10 mm notch was cut into each sample with a diamond saw. The samples and single edged razors were placed in a freezer overnight (approximately -20 °C) to ensure all samples were well within their glassy region when starter cracks were made. Samples and razor blades were removed from the freezer; the razor was inserted into the notch and tapped with a hammer, until a crack propagated into the sample 9 mm long, leaving a ligament of approximately 12.7 mm for the crack to propagate through during testing. These cracks were of the “instantly propagated” type, shown by Ma et al. to give minimum $K_{1c}$ values.
Samples were tested at -20 °C, 0 °C, 23 °C, or 40 °C after being conditioned at those temperatures for at least 2 hours. Seven samples per test condition were tested, unless noted otherwise, and the average of the measurements was reported.

3.3 Results & Discussion

3.3.1 Extent of Cure Analysis

Calculated heats of reaction for all samples were determined based on the measured heat of reaction of D230; these were compared to those measured. Since D230 is the shortest amine, the D230 resin is expected to have the least amount of steric hindrance and the most complete reaction. The heat of reaction for D230, \( \Delta H_{\text{cure, D230}} \), was used as a reference to calculate \( \Delta H_{\text{cure}} \) for the other resins. Theoretical heats of reaction for each resin were calculated by multiplying the reference \( \Delta H_{\text{cure, D230}} \) (521 J/g) by the ratio of the concentration of epoxy groups in each resin to the concentration of epoxy groups in the D230 resin, as shown in equation 3.24. The measured and calculated \( \Delta H_{\text{cure}} \) are listed in Table 3.2, and were similar in all cases. Also, no residual exothermic peaks were visible in any samples, signifying near complete reaction/cure. Full reaction, per DSC results, has also been reported for DGEBA reacted with short aliphatic amines [25-26].

\[
\Delta H_{\text{cure}} = \Delta H_{\text{cure, D230}} \times \frac{\text{mol Epoxy}}{\text{g resin}} \times \frac{\text{mol Epoxy}}{\text{g resin}_{D230}}
\] 3.24

NIR spectra of the uncured monomers clearly showed the peaks attributed to the amine and epoxy functional groups. These peaks were no longer visible in the spectra of
the cured samples, confirming the DSC results of complete reaction. When full conversion of epoxy resins is not achieved, residual secondary amine functional groups are evident in NIR spectra; however, this is more typical in higher T_g, aromatic-cured epoxy systems [4].

<table>
<thead>
<tr>
<th>Resin</th>
<th>ΔH_{cure} (measured) (J/g)</th>
<th>ΔH_{cure} (calculated) (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D230</td>
<td>521 ± 5</td>
<td>-</td>
</tr>
<tr>
<td>D400</td>
<td>458 ± 10</td>
<td>428</td>
</tr>
<tr>
<td>D2000</td>
<td>169 ± 8</td>
<td>183</td>
</tr>
<tr>
<td>B270 (D230)</td>
<td>500 ± 10</td>
<td>503</td>
</tr>
<tr>
<td>B390 (D230)</td>
<td>458 ± 15</td>
<td>449</td>
</tr>
<tr>
<td>B440 (D230)</td>
<td>429 ± 22</td>
<td>428</td>
</tr>
<tr>
<td>B620 (D400)</td>
<td>368 ± 19</td>
<td>372</td>
</tr>
<tr>
<td>B1000 (D230)</td>
<td>291 ± 7</td>
<td>288</td>
</tr>
<tr>
<td>B1000 (D400)</td>
<td>287 ± 2</td>
<td>288</td>
</tr>
</tbody>
</table>

### 3.3.2 FTIR Reaction Kinetics

The main purpose of characterizing the reaction kinetics of these systems is to measure the reactivity ratio: \( \frac{k_2}{k_1} \). A reactivity ratio of 0.5 implies that both the primary and secondary amines react equally, resulting in a completely random network [27] while a ratio <0.5 implies a substitution effect occurs where the consumption of a primary amine decreases the reactivity of the secondary amine, resulting in linear chains forming first which are cross-linked later in the reaction. In particular the reactivities of D400
compared to B440 are of interest and whether the blending of amines influences the formation of the network.

Omnic software is used to collect and analyze data. Figure 3.4 shows the evolution of the spectra as the reaction progresses. The peak at 5984 cm\(^{-1}\) is from the C-H stretching overtone on the bisphenol ring and is used as an internal reference except in the case of 825-D2000 where it was too weak; instead the peak at 4620 cm\(^{-1}\) was used [5, 8]. The conversion, \(\alpha\), of the epoxy is then found from the height of the epoxy peak at time \(t\), compared to the height at time 0, normalized to the height of the reference peak, equation 3.25:

\[
\alpha = 1 - \left( \frac{ABS(t)_{\text{peak}}}{ABS(t = 0)_{\text{peak}}} \right) \left( \frac{ABS(t = 0)_{\text{ref}}}{ABS(t)_{\text{ref}}} \right)
\]

where \(ABS(t)_{\text{peak}}\) is the absorbance of the peak at time \(t\), while the subscripts \(\text{ref}\) and 0 refer to the reference peak and initial time. For the amine peak, the peak area is used instead, as the spectra change dramatically around that peak. A small peak at 4566 cm\(^{-1}\), also identified in Figure 3.4, prevents the area of the epoxy peak from being used. The stability of the 5984 cm\(^{-1}\) reference peak meant that either its height or area was suitable as a reference; only the height was used.
Figure 3.4: Select spectra of 825-D400 as the cure reaction occurs. The epoxy, primary amine, and reference peaks were tracked; the epoxy and amine peaks shrink over time while the hydroxyl peak grows.
In conjunction with the FTIR data, the initial reactant concentrations are necessary to calculate the rate constants. The initial, unreacted, concentrations are calculated based on the actual sample masses, the components’ densities at 80 °C, and the assumption of no volumetric change of mixing. The Jeffamines’ densities at 80 °C were extrapolated from their published densities [28] at 25 °C using the behavior of propylene glycol [29] while the density of 825 at 80 °C was estimated from manufacturer literature [30]. The first spectrum taken is ignored due to the sample still heating up and some reaction will take place during mixing, therefore the initial concentrations must be adjusted before fitting the data. A calibration curve was created using various mixtures of 825 and JeffOx400. JeffOx400 is polypropylene glycol with approximate molecular weight of 400 g/mol, in essence the glycol version of Jeffamine D400. The calibration curve is shown in Figure 3.5 and shows the linear correlation between the height of the 4528 cm⁻¹ epoxy peak and the height of the 5984 cm⁻¹ reference peak; the calibration curve breaks down at low concentrations of 825 as the peak at 5984 cm⁻¹ is very faint or non-existent. The calibration curve does not extend to the concentration of epoxy in 825-D2000 due to its low epoxy concentration. Instead it was assumed that negligible reaction had taken place in D2000 samples. The height of the 5984 cm⁻¹ peak of the second spectrum of each sample was used to predict the height of the 4528 cm⁻¹ peak if no reaction had taken place. The difference in heights of the 4528 cm⁻¹ peak between the actual spectra and the height calculated from the calibration curve are interpreted to be the result of reaction. The reaction is presumed to be epoxy groups by reacting only with primary amines, and the initial concentrations are adjusted accordingly.
The primary amine and epoxy concentrations are used to calculate the secondary and tertiary amine concentrations following equations 3.3 and 3.4. The resulting concentration profiles are fit to equations 3.12 to 3.15 using the Matlab code shown in Appendix A. The data are fit only up to or just past the peak in the secondary amine concentration. After that point, gelation occurs and diffusion limitations alter the rate constants [4]. For the fitting procedure, the error is minimized with respect only to the epoxy and primary amine concentrations, as those are the experimentally measured
values. Figure 3.6 shows the experimental concentrations and the fit for one sample of 825-D400 while Table 3.3 shows the calculated rate constants.

Figure 3.6: Experimental data (points) and fits (lines) of 825-D400.
Table 3.3: Calculated rate constants at 80 °C.

<table>
<thead>
<tr>
<th>Resin</th>
<th>$k_1$ (L$^2$ mol$^{-2}$ min$^{-1}$)</th>
<th>$k_2$ (L$^2$ mol$^{-2}$ min$^{-1}$)</th>
<th>$k_2/k_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>D230</td>
<td>0.01305</td>
<td>0.00177</td>
<td>0.136</td>
</tr>
<tr>
<td></td>
<td>0.01125</td>
<td>0.00165</td>
<td>0.147</td>
</tr>
<tr>
<td>D400</td>
<td>0.01045</td>
<td>0.00125</td>
<td>0.120</td>
</tr>
<tr>
<td></td>
<td>0.01205</td>
<td>0.00093</td>
<td>0.077</td>
</tr>
<tr>
<td>D2000</td>
<td>0.01050</td>
<td>0.00132</td>
<td>0.125</td>
</tr>
<tr>
<td></td>
<td>0.01005</td>
<td>0.00087</td>
<td>0.087</td>
</tr>
<tr>
<td>B440</td>
<td>0.01190</td>
<td>0.00131</td>
<td>0.110</td>
</tr>
<tr>
<td></td>
<td>0.00900</td>
<td>0.00077</td>
<td>0.086</td>
</tr>
<tr>
<td></td>
<td>0.01265</td>
<td>0.00116</td>
<td>0.092</td>
</tr>
</tbody>
</table>

The $k_1$ rate constant for all the resins are similar, as is to be expected given the similar structure of the amine. The reactivity of the secondary amine in D230 appears to be slightly higher than for all the other resins, resulting in a reactivity ratio of ~0.14 compared to ratios of 0.08-0.13 for the other resins. Mijovic reported reactivity ratios for a variety of epoxies and amines [27]. Those ratios varied widely, even for the same system, for example DGEBA with DDS had reported ratios of 0.5 and 0.1, albeit using different methods. Using methods most similar to the ones used here, Raman and Palmese reported reactivity ratios for an DGEBA-PACM system that decreased with increasing temperature, from 0.28 at 40 °C to 0.19 at 60 °C [7]. The values presented here are in line with those, assuming the decreasing trend with increasing temperature holds. Unlike those collected by Mijovic and reported by Raman and Palmese, the amines used here are of increasing molecular weight. The slight decrease in the reactivity ratio for amines longer than D230 could be due to steric hindrance due to the molecular weight increase if only the D230 is short enough to prevent backbone
interactions. D230 has almost half the backbone atoms as D400 and one tenth that of D2000; however, of main interest for this work is that B440 and D400 have similar rate constants, implying that those networks form in similar manners.

### 3.3.3 Thermomechanical Properties

Table 3.4 and Table 3.5 summarize the DMA and density results for the resin blends, with the breadth of transition being reported as the full width at half maximum of the tan δ curve; the properties had narrow distributions and no batch-dependent variations were observed provided stoichiometry was maintained. The room temperature densities steadily decrease as the average amine molecular weight increases and as the T_g of the resins decreases. The density-temperature curves from CTE and measured density values are plotted in Figure 3.7, shifted to T-T_g, using the peak of the loss curve as the T_g. The inflection in CTE, and hence density, data is also a measure of the T_g but here the inflections in the curves do not match up with 0 as different thermal lags exist between the CTE and DMA data due to the different sample dimensions and heating ramp rates. When shifted to T-T_g, it is observed that formulations containing any amount of D230 approach a density of 1.165 g/cm³ 100 °C below their respective T_g's, while those containing D400 approach a lower density of 1.155 g/cm³. The sample containing only D2000 has the lowest density. While CTE data was not available for the B1000 blends, their measured room temperature densities are also plotted in Figure 3.7 and it appears they would follow the same trends as the other blends.
Figure 3.7: Density as a function of $T - T_g$ from CTE data. The dotted line for D2000 is a linear extrapolation to $T - T_g = -100$ for comparison.

Table 3.4: Summary of density

<table>
<thead>
<tr>
<th>Resin</th>
<th>Density at 25 °C (g/cm$^3$)</th>
<th>Glassy Density ($T_g$-30 °C) (g/cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D230</td>
<td>1.157 ± 0.001</td>
<td>1.146 ± 0.001</td>
</tr>
<tr>
<td>D400</td>
<td>1.138 ± 0.002</td>
<td>1.138 ± 0.002*</td>
</tr>
<tr>
<td>D2000</td>
<td>1.060 ± 0.010</td>
<td>1.126 ± 0.011</td>
</tr>
<tr>
<td>B270 (D230)</td>
<td>1.153 ± 0.002</td>
<td>1.143 ± 0.002</td>
</tr>
<tr>
<td>B390 (D230)</td>
<td>1.145 ± 0.001</td>
<td>1.141 ± 0.001</td>
</tr>
<tr>
<td>B440 (D230)</td>
<td>1.140 ± 0.009</td>
<td>1.139 ± 0.009</td>
</tr>
<tr>
<td>B620 (D400)</td>
<td>1.125 ± 0.000</td>
<td>1.137 ± 0.000*</td>
</tr>
<tr>
<td>B1000 (D230)</td>
<td>1.094 ± 0.001</td>
<td>N/A</td>
</tr>
<tr>
<td>B1000 (D400)</td>
<td>1.096 ± 0.001</td>
<td>N/A</td>
</tr>
</tbody>
</table>

*only one sample available for CTE measurements
Table 3.5: Summary of DMA results

<table>
<thead>
<tr>
<th>Resin</th>
<th>Modulus at 30 °C (MPa)</th>
<th>30 °C (°C)</th>
<th>Peak of Tan δ (°C)</th>
<th>Breadth of transition (°C)</th>
<th>Tβ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D230</td>
<td>2360 ± 70</td>
<td>91.9 ± 2.8</td>
<td>97.9 ± 2.2</td>
<td>11.2 ± 0.8</td>
<td>-59</td>
</tr>
<tr>
<td>D400</td>
<td>2370 ± 110</td>
<td>53.8 ± 0.3</td>
<td>59.0 ± 0.4</td>
<td>10.2 ± 0.4</td>
<td>-68</td>
</tr>
<tr>
<td>D2000</td>
<td>2.0 ± 0.1*</td>
<td>-37.4 ± 0.7</td>
<td>-24.1 ± 1.0</td>
<td>19.9 ± 1.8</td>
<td>-85</td>
</tr>
<tr>
<td>B270 (D230)</td>
<td>2460 ± 30</td>
<td>85.3 ± 1.2</td>
<td>92.7 ± 1.1</td>
<td>12.9 ± 0.6</td>
<td>-53</td>
</tr>
<tr>
<td>B390 (D230)</td>
<td>2080 ± 40</td>
<td>61.7 ± 1.5</td>
<td>75.5 ± 0.3</td>
<td>19.5 ± 0.5</td>
<td>-63</td>
</tr>
<tr>
<td>B440 (D230)</td>
<td>1740 ± 100</td>
<td>55.6 ± 0.8</td>
<td>69.8 ± 0.4</td>
<td>21.5 ± 0.5</td>
<td>-64</td>
</tr>
<tr>
<td>B620 (D400)</td>
<td>640 ± 50</td>
<td>28.2 ± 1.2</td>
<td>41.8 ± 0.3</td>
<td>16.5 ± 0.5</td>
<td>-71</td>
</tr>
<tr>
<td>B1000 (D230)</td>
<td>9.4 ± 0.9</td>
<td>-26.9 ± 0.9</td>
<td>16.2 ± 0.9</td>
<td>37.2 ± 0.4</td>
<td>-76</td>
</tr>
<tr>
<td>B1000 (D400)</td>
<td>6.9 ± 0.8</td>
<td>-18.9 ± 1.2</td>
<td>13.6 ± 2.0</td>
<td>23.4 ± 1.0</td>
<td>-73</td>
</tr>
</tbody>
</table>

*values from thick DMA samples

As mentioned previously, the temperature of the peak in the DMA loss modulus was used at the Tg. The loss modulus is plotted versus T-Tg in Figure 3.8. The main or α relaxation is the glass transition, Tg, whereas the secondary or β transition is also visible; both are listed in Table 3.5. The beta relaxation (Tβ) for epoxy resins is attributed to the relaxation of the hydroxypropyl ether units [-O-CH2-CH(OH)-CH2-] and is known to occur between −60 °C and −100 °C [31-32]. All Tβ for these resins appear in that range. The epoxy Tβ is known to shift to lower temperatures as the network changes from a highly cross-linked to a more linear polymer [33]; the same trend is observed here, with D2000 having the lowest Tβ and D230 the highest. The magnitude of the beta peak in the loss modulus also decreases as the concentration of the hydroxypropyl ether groups decreases, with D230 having the strongest transition and B1000 (D230), B1000 (D400) and D2000 all have very weak transitions.
Comparing the resins with single amines, the D2000 exhibits the largest loss modulus, followed by D400 and D230, whereas the opposite is seen in the T_g's, with D2000 having the lowest. While the magnitude of the loss peak for the blends does not follow a trend, there is a trend of decreasing T_g with increasing average amine molecular weight. For some samples, especially B390 (D230), B440 (D230), and B620 (D400) a third peak or shoulder appears in the loss modulus around −20 °C. This peak is near that of D2000 (-37 °C) and suggests there is micro-phase separation with a D2000-rich phase, however since these samples are optically clear, the domains must be small.
Comparing the breadth of tan δ at half maximum, as listed in Table 3.5, to the storage modulus curves in Figure 3.9, the breadth of the tan δ at half maximum appears to be a reasonable measure of the breadth of the glass transition. D230, D400, and B270 (D230) all reached their rubbery region at about the same temperature, ~10 °C above T_g and all had similar breaths of transitions. B390 (D230), B440 (D230), B620 (D400), and D2000 all reached their rubbery regions about 20 °C above T_g, which is reflected in full width at half maximum tan δ values of approximately 20 °C. Both B1000 blends did not
reach their rubbery regions until 25-40 °C above Tg. All of the tan δ curves are shown in Figure 3.10, plotted against T-Tg. This figure also shows that in blends with higher D2000 content, the tan δ peak is shifted to higher temperatures relative to the Tg due to the increased broadness of the transition. Here it appears that certain blends of low and high molecular weight polyetheramines can greatly broaden the glass transition without changing its location.

![Figure 3.10: Tan δ curves for all resins, plotted versus T-Tg.](image)

To easily view modulus trends, the modulus data were plotted versus T-Tg, and are shown in Figure 3.9. With regards to the single amine resins, there was a trend of
higher glassy modulus with increasing amine molecular weight at a given distance below \( T_g \). This trend was seen elsewhere for epoxies cured with D230 and D400 [34]. At a given offset below the \( T_g \), as the amount of D2000 increased, the glassy modulus increased. At 75 °C below \( T_g \), the resins containing mostly D230 or D400 appeared to reach a plateau of 2500-3000 MPa while those containing more D2000 tracked towards or reached a plateau of 3500-4000 MPa. As mentioned earlier, the densities decreased with increasing D2000 content, so improved packing at lower temperatures does not explain the increased modulus. The increase in modulus with increasing amine molecular weight can be partially attributed to hydrogen bonding which can increase modulus values and is stronger at lower temperatures [35]. As the molecular weight of the amines increased, the number of hydroxyl groups and hence hydrogen bonds decreased; however, amine flexibility and the number of oxygens that can act as hydrogen acceptors also increased in addition there may be more residual hydroxyls present in the D2000. Figure 3.11 shows the network structure of these resins, as \( n \) increases in the polyetheramines, the backbone oxygens have more flexibility to act as hydrogen acceptors. Increased polyether flexibility is known to increase the extent of hydrogen bonding [36]. The modulus increase is also affected by the reduced \( T_g \)s. The resins with the highest moduli at 50 °C below \( T_g \), D2000, B1000 (D230) and B1000 (D400), also have the lowest \( T_g \)s. At 50 °C below \( T_g \) for these resins is also below the beta relaxation of epoxies, −50−−70 °C, and the freezing of the hydroxypropyl ether units can increase the modulus [31].
Three pairs of resins invite comparisons. The D230 and B270 (D230) resins had the highest and very similar $T_g$s, which was unsurprising given that the bimodal amine blend was over 85 wt% or 92 mol% D230. Interestingly, the storage modulus for the B270 (D230) blend is higher than that of D230 below 50-60 °C ($T - T_g \sim -25 \ °C$), but lower at higher temperatures (Figure 3.9). This modulus crossover cannot be explained by density variations, as the density for the D230 had the highest density at any temperature, as shown in Figure 3.7, nor $T_\beta$ relaxations as this crossover is well above the $T_\beta$ transitions. Instead the modulus crossover can be partially attributed to additional
hydrogen bonding [33-34]; the B270 (D230) has approximately 20% more backbone oxygens than D230.

The B440 (D230) blend and D400 had the same AHEW and consequentially had the same \( T_g \), though the blend had a broader glass transition. The storage modulus of the blend was approximately 1 GPa lower at 30 °C (\( T - T_g \sim -25 \) °C), but exceeded that of D400 at \( T - T_g \sim -60 \) °C. The breadth of the transition for the B440 (D230) was twice as broad as that of the D400 alone, and similar to that of D2000. Above \( T_g \), the density of B440 (D230) was lower than that of D400; however, below \( T_g \), B440 (D230) had a higher density. This density crossover occurs at \( T - T_g \sim -30 \) °C, approximately 30 °C away from the modulus crossover. Despite the different crossover locations, the increased density at lower temperature can contribute to the higher modulus at lower temperature. In addition, different thermal lags due to the different sample dimensions and heating ramp rates in the thermomechanical analysis relative to DMA testing may also contribute to the crossover difference.

The two blends with AHEW values matching a hypothetical D1000 were less similar than expected. Their \( T_g \)s differed by approximately 10 °C and the breadth of the transition was \( \sim14 \) °C broader for the blend using D230 rather than D400. The B1000 (D230) resin contained more D2000 than any other bimodal blend and consequentially could have had more intramolecular cyclization during cure than the others.

The Fox equation, equation 3.26, predicts the \( T_g \) of a blend of polymers based on the individual glass transition temperature of the components \( i, T_{gi} \), along with the weight fractions, \( w_i \)[37]:

\[ T_g = \frac{\sum w_i T_{gi}}{\sum w_i} \]
\[
\frac{1}{T_g} = \frac{w_a}{T_{ga}} + \frac{w_b}{T_{gb}}
\]  

By treating the blends as mixtures of 825/D2000 with 825/D230 or 825/D400, the Fox equation gives reasonably good predictions, although it requires separate calculations for the D400 and the D230 blends, generating two curves. Instead, if \( T_g \) is plotted versus the volume fraction of amine, based upon uncured liquid volumes, a single linear trend is obtained, as shown in Figure 3.12. The largest deviation from the linear trend comes with the B1000 blends, which could be due to increased heterogeneity as the content of D2000 increased.
The breadth of the $T_g$ increased with increasing amount of D2000 in the blends; however, it was not a simple function of D2000 content. The broadening of the transition is often associated with heterogeneity in the network structure with different segments having low and high $T_g$'s [12]. This is exhibited by the fact that B440 (D230) had a significantly broader glass transition than B620 (D400) while both had similar D2000 content. When plotted against the volume fraction of amine, it becomes clear that the breadth is dependent upon both the amine volume fraction as well as the type of amine, as shown in Figure 3.13.

Figure 3.12: $T_g$ and total damping vs. volume fraction of amine.
Figure 3.13: Breadth of $T_g$ vs. total amine volume fraction. The narrowest breaths of each line are from single amine resins.

In addition to broadening the tan $\delta$, the blends also have decreased maximum dampening compared to the single amine resins. Even though the maximum damping is decreased, the total damping capacity increased with increasing amine molecular weight. The total damping was calculated by integrating the tan $\delta$ curves. Instead of specifying a temperature range to integrate, the integration limits were set at the temperatures where tan $\delta$ equaled 0.05 on either side of the tan $\delta$ peak. Increased damping means that the blends are more able to dissipate energy through viscous means than their single amine
counterparts [12]. The total damping is also directly proportional to the amine volume fraction, as shown in Figure 3.12. The tan δ area is known to decrease with increasing cross-linking level and $T_g$ for polyacrylates and it applies to these epoxy-amine networks as well [38]. The linear relationship and the similar damping of D400 and B440 (D230) suggests that, neglecting stoichiometry, a single D2000 molecule has similar damping compared to several molecules of D230 of equivalent molecular weight.

### 3.3.3.1 Cross-Link Density

There is a very strong trend of increased $M_c$ with increased amine molecular weight. The experimental $M_c$ values were calculated using eq. 3.16 and plotted in Figure 3.14 against the average amine molecular weight. The values for the moduli used in eq. 3.16 were taken from the minimum modulus value, whose location ranged from 26 to 82 °C above $T_g$ for the narrowest and broadest transitions, D400 and B1000 (D230) respectively. The temperature appropriate densities, as calculated by the CTE measurements were used except for the B1000 (D230) & B1000 (D400) resins. Their densities were estimated to be 1.05 and 1.06 g/cm$^3$, respectively, based on their room temperature densities, the trends from the other formulations, and the distance above $T_g$ at which those minima occurred. The $M_c$ values are summarized in Table 3.6.
Figure 3.14: Experimental and theoretical $M_c$ values versus average amine molecular weight. The short dashed line represents eq. 3.28 and the solid line eq. 3.29.

Table 3.6: Experimental $M_c$ and theoretical $M_c$ values calculated using equations 3.29 and 3.30 and the number of loop defects necessary to match the data.

<table>
<thead>
<tr>
<th>Resin</th>
<th>$M_c$ (experimental) (g/mol)</th>
<th>$M_c$ (theo) (eq. 3.29) (g/mol)</th>
<th>$M_c$ (single loop) (eq. 3.30) (g/mol)</th>
<th>Number of Loops Required</th>
</tr>
</thead>
<tbody>
<tr>
<td>D230</td>
<td>593 ± 25</td>
<td>315</td>
<td>629</td>
<td>0.94 ± 0.04</td>
</tr>
<tr>
<td>B270 (D230)</td>
<td>632 ± 13</td>
<td>325</td>
<td>649</td>
<td>0.97 ± 0.02</td>
</tr>
<tr>
<td>B390 (D230)</td>
<td>791 ± 14</td>
<td>365</td>
<td>729</td>
<td>1.07 ± 0.02</td>
</tr>
<tr>
<td>B440 (D230)</td>
<td>826 ± 44</td>
<td>381</td>
<td>763</td>
<td>1.08 ± 0.06</td>
</tr>
<tr>
<td>D400</td>
<td>798 ± 21</td>
<td>383</td>
<td>765</td>
<td>1.04 ± 0.03</td>
</tr>
<tr>
<td>B620 (D400)</td>
<td>950 ± 54</td>
<td>441</td>
<td>883</td>
<td>1.08 ± 0.06</td>
</tr>
<tr>
<td>B1000 (D400)</td>
<td>1553 ± 111</td>
<td>568</td>
<td>1136</td>
<td>1.31 ± 0.10</td>
</tr>
<tr>
<td>B1000 (D230)</td>
<td>1762 ± 143</td>
<td>567</td>
<td>1133</td>
<td>1.47 ± 0.12</td>
</tr>
<tr>
<td>D2000</td>
<td>4013 ± 195</td>
<td>895</td>
<td>1789</td>
<td>2.24 ± 0.11</td>
</tr>
</tbody>
</table>
The D400 and B440 (D230) samples had nearly the same $M_c$, which was expected as the blend was designed to match D400. The $M_c$ values of B1000 (D400) are also very similar, despite having $T_g$s almost 10 °C apart.

Theoretical $M_c$ values can be calculated in several ways. Scanlan calculated the molecular weight between cross-links using equation 3.27 [39-40]:

$$M_c = \frac{W}{\sum_{f=3}^{\infty} \frac{f}{2} C_f}$$  \hspace{1cm} 3.27

where $W$ is the weight of the network repeat unit, $f$ is the functionality of the reactant, and $C_f$ is the number of reactants $f$ present in the repeat unit. This is simply the molecular mass of the repeat unit, divided by the number of network chains. Charlesworth stated that a short rigid diamine can effectively be considered a tetrafunctional point, $f = 4$ (2 network chains), otherwise a diamine should be considered to be two tri-functional blocks, $f = 3$, ensuring that the backbone between the amine groups is considered as a network chain (3 network chains) [41]. In these two cases, $M_c$ is given by eq. 3.28 and eq. 3.29, respectively, and the repeat unit can be depicted as shown in Figure 3.15:

$$M_c = \frac{M_{\text{amine}} + 4 \times \left(\frac{1}{2} \cdot M_{\text{epoxy}}\right)}{2}$$  \hspace{1cm} 3.28

or

$$M_c = \frac{\frac{1}{2} M_{\text{amine}} + 2 \times \left(\frac{1}{2} \cdot M_{\text{epoxy}}\right)}{3/2} = \frac{M_{\text{amine}} + 4 \times \left(\frac{1}{2} \cdot M_{\text{epoxy}}\right)}{3}$$  \hspace{1cm} 3.29
The Jeffamines have backbone lengths varying from approximately 11 atoms for D230 to approximately 103 for D2000, so given the flexible backbone, each amine molecule should be considered to be two tri-functional bodies and $M_c$ should be governed by eq. 3.29. Additionally, these equations agree with the theory of Miller & Macosko [42], whose theory reduces to Scanlan’s in the limit of complete reaction, as was measured for these epoxy-amine resins systems.

Figure 3.14 also shows the results of equations 3.28 and 3.29. While the experimental data is closer to that of equation 3.28, the larger amine molecules cannot be assumed to act as tetrafunctional points. Some work has measured $M_c$ in epoxies to be similar to the theoretical value calculated by eq. 3.29. LeMay used DGBEA reacted with 4,4’-diaminodiphenyl sulfone (DDS) and measured slightly lower than expected $M_c$s [43], possibly due to steric restrictions due to the bulky and rigid aromatic rings [41]. Nakka et al. reacted a variety of short linear $f$ functional amines with DGEBA and saw good agreement between theoretical values calculated in a method similar to eq. 3.28 and measured low values of $M_c$ with amines containing 3-4 amine hydrogens, but the disagreement increased with increasing $M_c$ as the number of amine hydrogens decreased.
Crawford & Lesser also had good agreement between theoretical and experimental values for stoichiometric blends of either linear or aromatic tri-functional amines and also for tetrafunctional amines but only for theoretical $M_c$ values greater than 500-600 g/mol.

In this work the agreement between theoretical and experimental $M_c$s is poorer and the difference increased with increasing amine molecular weight. In all the above mentioned cases, the amines used were either aromatic or very short linear chains. Here we have longer, flexible amines that are more mobile. Network mobility is often accounted for using the “phantom network” model, in which no physical interactions between adjacent chains are considered [44-45]. This model modifies the $M_c$ calculation (eq. 3.16) with a $\frac{f-2}{f}$ term, where $f$ is the functionality of the cross-linking molecule, in this case $f = 3$. The results of applying this front factor to the experimental $M_c$ calculations are also shown in Figure 3.14. The phantom network assumption reduces $M_c$ below either of the two structural models for $M_c$. Since the assumption removes any physical interactions, it is often coupled with other terms that add back in the contributions of chain entanglements and non-Gaussian chain statistics [41, 43]. Adding these contributions back will bring the $M_c$ values in the range predicted by the structural model. More interesting is the fact that the experimental $M_c$ values appear to follow two trends. Resins with amine blends 620 g/mol and below follow a slope that is similar to the model predictions, presumably because those networks have relatively few defects, while the slope of those formulations with amine blends greater than 620 g/mol is much steeper. This deviation can be explained by cyclization. As the amount of D2000
increases in a resin, the potential for cyclization increases as the large molecule can bend around and react with the same epoxy or possibly creating small self-contained areas in the network. These defects can substantially increase $M_c$; a simple single loop defect of D2000, as shown in Figure 3.16, would increase $M_c$ by approximately 900 g/mol. If a single loop defect is considered, then eq. 3.29 becomes:

$$M_c = \frac{2 \times M_{\text{amine}} + 4 \times \left(\frac{1}{2} \times M_{\text{epoxy}}\right) + 2 \times M_{\text{epoxy}}}{3}$$

3.30

Figure 3.16: Sketch showing a single loop defect. Dashed lines represent epoxies, while solid represent amines; arrows extend out into the bulk network.

And the results, shown in Table 3.6 and Figure 3.14, match well with the experimental values for the lower molecular weight amines, suggesting that some defects occur even with the smaller amines. By dividing the experimental $M_c$ by the values calculated assuming a single loop defect, the number of defects can be estimated. These results are also shown in Table 3.6. There is still a large departure above B620, with the
number of defects increasing to over two, indicating that large amounts of D2000 can introduce many defects into the networks.

The resins in other works that were well predicted by eqs. 3.28 or 3.29 were very different, structurally, compared to the resins used here. This shows that flexible amines can dominate the network properties when paired with shorter more rigid epoxies, although more defects occurred when the length of the flexible amine increased.

3.3.3.2 TTS

The shift factors were found manually, by graphically shifting the curves until overlap was achieved; below \( T_g \) the storage modulus was fit, while above \( T_g \), the loss modulus was fit. The resulting storage and loss master curves are shown in Figure 3.17 and Figure 3.18. That fact that both sets curves are generated by the same shift factors, per resin, implies that TTS is applicable for these resins [16]. The storage master curve is almost the reversed image of the storage modulus versus \( T - T_g \) curves shown in Figure 3.9. Figure 3.19 shows a portion of the master curve with the frequency axis reversed directly compared to the temperature ramp DMA results. The modulus values do not precisely align, but the order does. The two types of tests were performed with different DMA sample thicknesses and different thermal histories, better modulus agreement could perhaps be obtained if the same thicknesses for all samples were used or if the temperature ramp rate was reduced for the 1 Hz samples. This general similarity also reinforces that fact that the assumptions of TTS are applicable to these resins.
Figure 3.17: Storage master curve.
Figure 3.18: Loss master curve.

Figure 3.19: Storage modulus vs. $T - T_g$ (left) compared to master curves using $T_g$ as a reference (right).
The temperature of the relaxation rarely coincided with one of the temperature steps. To find the actual temperature of the relaxation, interpolation or peak fitting was required. For discrete peaks, Omnic (Thermo-Fisher), a spectroscopic program, was used to increase the resolution and find the peak maxima and hence the relaxation temperatures. Figure 3.20 shows the data points around the $T_g$ for B270 at 1 Hz, along with Omnic interpolations at a resolution of 1 and a resolution of 0.125. The temperatures of the peak maxima as determined using Omnic with a resolution of 0.125 were used in eq.3.21.

Figure 3.20: Raw data and Omnic interpolations used to find the temperature of the maximum.
When the $T_g$ overlapped with either $T_\beta$ or other transitions, Igor Pro (Wavemetrics) was used to deconvolute the peaks. The main peak in the loss modulus was best fit by an “ExpModGauss” curve, which is the convolution between a Gaussian curve and an exponential decay, while other transitions were well fit by Gaussian curves.

From the obtained the shift factors, the constants $c_1^0$ and $c_2^0$ were then determined by two methods: by minimizing the least squares error when fit to equation 3.19 and from the slope and intercept of the best fit line from a linearization of the WLF equation, eq. 3.31:

$$\frac{-1}{\log a_T} = \frac{c_2^0}{c_1^0} \left( \frac{1}{T - T_0} \right) + \frac{1}{c_1^0}$$

It is generally reported that the WLF equation is valid from $T_g$ to $T_g + 100 \, ^\circ C$ [21]; however when calculating $c_1^0$ and $c_2^0$ by the least squares method, only data from $T_g - 3 \, ^\circ C$ to $T_g + 30 \, ^\circ C$ were used, referring to the $T_g$ at 1 Hz. The few points below $T_g$ were included because the reference curve did not always coincide perfectly with the actual $T_g$. Above approximately $T_g + 30 \, ^\circ C$ often one or more data points per frequency sweep were invalid, i.e. negative storage or loss values. These negative values, along with their complementary storage or loss modulus value, were removed before shifting the curves. Another reason the data from above $T_g + 30 \, ^\circ C$ were not included is due to the instrument stiffness/sensitivity concerns as described in Chapter 2, and the difficulty in obtaining accurate shift factors for almost constant storage and loss moduli. By restricting the analysis to $T_g + 30 \, ^\circ C$, the unreliable rubbery region associated with DC and thin SC samples should have been avoided. In addition, $c_1^0$ and $c_2^0$ of the thicker SC samples of D230 and D400, which have valid data throughout the rubbery region,
matched well with those calculated for thinner or DC samples. For the constants calculated from 3.31, shift factors up to the first invalid data were included. The constants are summarized in Table 3.7. With the exception of B390, none of the constants are similar to the initially termed “universal constants” [21]; however, their values are of similar magnitude of other polymers [16]. B1000-D230 had the largest difference in constants between the two methods. This resin was a rare sample that did not have any invalid data for most of its rubbery region, up to $T_g + 80$ °C, so the difference could be due to the much larger number of data points used in the linearized method compared to the least squares fit.

Table 3.7: Calculated WLF constants.

<table>
<thead>
<tr>
<th>Resin</th>
<th>Linearized WLF</th>
<th>Least Squares Fit</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$c_1^0$</td>
<td>$c_2^0$ (°C)</td>
</tr>
<tr>
<td>D230</td>
<td>8.2 ± 0.5</td>
<td>33.9 ± 3.4</td>
</tr>
<tr>
<td>B270</td>
<td>9.5 ± 0.1</td>
<td>35.3 ± 7.7</td>
</tr>
<tr>
<td>B390</td>
<td>15.1 ± 0.8</td>
<td>59.0 ± 1.3</td>
</tr>
<tr>
<td>D400</td>
<td>9.4 ± 1.1</td>
<td>38.5 ± 8.9</td>
</tr>
<tr>
<td>B440</td>
<td>24.5 ± 6.4</td>
<td>116.3 ± 34.7</td>
</tr>
<tr>
<td>B620</td>
<td>11.5 ± 1.6</td>
<td>44.1 ± 7.7</td>
</tr>
<tr>
<td>B1000-D230</td>
<td>37.2</td>
<td>177</td>
</tr>
<tr>
<td>B1000-D400</td>
<td>23.2</td>
<td>100.0</td>
</tr>
<tr>
<td>D2000</td>
<td>12.2 ± 0.9</td>
<td>50.1 ± 0.5</td>
</tr>
</tbody>
</table>

Activations energies of the $T_g$s were then calculated from the constants. In some cases the activation energies calculated by both methods, eq. 3.20 and eq. 3.21 agree quite well [46]. In other cases the plot of $\ln f$ vs. $1/T$ is best described by a second order polynomial [47] rather than a straight line. For a polyetherimide, fitting $\ln f$ versus the
peak in the tan δ over the range of 0.1-10^5 Hz from dielectric spectroscopy or 0.01 – 200 Hz from DMA resulted in a second order polynomial and therefore non-constant activation energy. In this work the plots of ln f vs. 1/T are linear.

The calculated activation energies for the T_g are shown in Figure 3.21. The energies from the WLF equation, regardless of how the constants were determined, were similar, including those for B1000-D230. In general there is a trend of decreasing ΔH_a with increasing average amine molecular weight. The only exception is that B1000-D400 has an activation energy greater than B1000-D230; however, given the standard deviations for D230 and D400, similar sized deviations for the B1000 blends, would yield no significant difference in ΔH_a. For most resins, both Arrhenius and WLF methods yield similar ΔH_a values, the exceptions are the D230, B390, and D400. For D230 and D400 the ΔH_a from the Arrhenius T_g shift are higher than those calculated from the WLF equation, while for B390 the ΔH_a from the T_g shift is lower. Given the relatively small sample sizes analyzed here, it is impossible to conclusively say if these three differences are significant.
In the prior section all of these blends show beta transitions in the -60 – -85 °C range when tested at 1 Hz with a 2 °C/min temperature ramp, although those for the D2000 and B1000 blends are very subtle. During the stepwise isothermal frequency sweeps, the beta transitions were clearly evident for all resins except D2000 and the B1000 blends. In the D2000, for some frequencies, the beta transition was present only as a shoulder to the main transition, otherwise it was not visible at all. For the B1000 resins, no visible beta relaxations were seen when starting at -75 °C and tests at lower temperature were not performed. These transitions, along with the main $T_g$ are shown in Appendix B.
As mentioned previously, $T_\beta$ for epoxy resins is generally attributed to the relaxation of the hydroxypropyl ether units [-O-CH$_2$-CH(OH)-CH$_2$-] and is known to occur between $-60 \, ^\circ\text{C}$ and $-100 \, ^\circ\text{C}$ [31-32]. More recently it has been suggested that the beta transition is actually several overlapping transitions, two of which are separated by only 7 kJ/mol: the trans-gauche isomerization of the methylene groups and the $\pi$ flip of the phenyl rings [33]. The epoxy $T_\beta$ is also known to shift to lower temperatures as the network changes from a highly cross-linked to a more linear polymer [33]. Table 3.8 lists the temperature range over which $T_\beta$ was observed for each resin, along with the activation energy. As mentioned previously for 1 Hz DMA runs, $T_\beta$ shifts to lower temperatures with increasing amine molecular weight as expected, and this holds for the multi-frequency runs. The activation energies for $T_\beta$ are similar to those seen for other epoxy systems [33, 48].
Table 3.8: Temperature range for transitions (0.1 – 50 Hz) and their activation energies.

<table>
<thead>
<tr>
<th>Resin</th>
<th>$T_g$ range (°C)</th>
<th>$\Delta H_a$ (kJ/mol) (Arrhenius Shift)</th>
<th>$T_\beta$ range (°C)</th>
<th>$\Delta H_{T_\beta}$ (kJ/mol)</th>
<th>$T_{int}$ range (°C)</th>
<th>$\Delta H_{int}$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D230</td>
<td>82 – 94</td>
<td>818 ± 39</td>
<td>-43 – -44</td>
<td>62 ± 4</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>B270</td>
<td>74 – 87</td>
<td>671 ± 24</td>
<td>-82 – -42</td>
<td>56</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>D400</td>
<td>42 – 54</td>
<td>648 ± 26</td>
<td>-79 – -47</td>
<td>56 ± 1</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>B620</td>
<td>16 – 28</td>
<td>432 ± 7</td>
<td>-96 – -55</td>
<td>48</td>
<td>-35 – -8</td>
<td>120</td>
</tr>
<tr>
<td>B1000-D230</td>
<td>-43 – -29</td>
<td>197</td>
<td>NA</td>
<td>NA</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>B1000-D400</td>
<td>-31 – -20</td>
<td>255</td>
<td>NA</td>
<td>NA</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>D2000</td>
<td>-50 – -38</td>
<td>266 ± 27</td>
<td>-92 – -79*</td>
<td>70</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

* $T_\beta$ could not be determined for all frequencies

NA: not available due to experimental temperature range

Dash indicates transition is not present

In addition to the beta transitions, several resins: B390, B440, and B620, had intermediate transitions, $T_{int}$, also described in Table 3.8. All of these transitions occur approximately 10 °C above D2000’s $T_g$, suggesting a D2000 rich phase. B440’s intermediate transition has a much higher activation energy compared to the other two and is very similar to that of D2000. The freezing of the molecular motions causing these intermediate transitions could explain the modulus crossover seen around -5 – 0 °C where B390 and B440 begin to exceed D400. Despite these apparent D2000-rich portions, as mentioned, the samples were all optically transparent.

D2000 was the only resin tested below -100 °C. This revealed a gamma transition for the epoxy appearing between -142 and -120 °C with energy of 36 kJ/mol. These are typical, in both location and energy, of relaxations caused by at least four $-CH_2-$ groups.
or a mixture of \(-\text{CH}_2-\) and \(-\text{O}-\) groups [49-50], such as are found in the Jeffamines’ backbone.

### 3.3.4 Fracture Toughness

Fracture toughness results are shown in Figure 3.23. D400, B390 (D230) and B440 (D230) had invalid (ductile tearing) results for 40 °C. After observing 1-2 samples tear, the remainder of those samples were reconditioned and tested at -20 °C.

There is a gradual increase in $K_{1c}$ as the testing temperature approaches the $T_g$s of the resins. The noticeable increases occur with the B270 (D230) tested at 40 °C and the D400 tested at 23 °C. The B270 (D230) appears to deviate from the trend but it was one of only two sets that were tested at elevated temperatures. Increased temperature decreases yield stress resulting in higher fracture toughness [3]. Some samples of both the D230 and B270 (D230) tested at 40 °C showed visible signs of plastic deformation. Those samples that showed obvious plastic deformation were not included in the analysis. Other samples, including the room temperature D400 and B440 (D230) samples, showed no visible deformation, despite being tested closer to their respective $T_g$s, suggesting that above ambient temperatures eases plasticization in these resins, regardless of $T_g$.

Few samples showed the ideal behavior of a linear load increase followed but an instantaneous drop as fracture occurred. Instead the behavior varied from brittle-stable crack growth, where the load increased linearly until fracture initiated in a slow, controlled manner with no evidence of ductility, to unstable crack growth where the load increased linearly until fracture initiated but then arrested one or more times, resulting in
“slip-stick” crack growth, shown in Figure 3.22. Some samples showed unstable crack growth with no arrest. The cracks were characterized as either stable (S), stable-unstable (S-U-SS) which showed both a crack arrest as well as slow propagation, unstable stick-slip (U-SS) which showed at least one arrest point, or unstable (U) characterized by sharp load decrease with no crack arrest. Similar transitions between types of crack growth with increasing temperature have been seen in other epoxy systems including amine-cured, anhydride-cure [51], and homopolymerized epoxies; this behavior was seen in both neat and rubber toughened homopolymerized epoxy [52].
Figure 3.22: Fracture behavior - A) stable (S), B) stable-unstable (S-U-SS), C) Unstable slip-stick (U-SS), D) Unstable (U), E) Ductile.
Figure 3.23: Fracture toughness data plotted vs. T - T_g. Symbols signify the formulations as indicated by the legend. Fracture type is indicated by color/fill: Orange: brittle-stable fracture; Blue: stable-unstable; Green: unstable-stick slip; Red: unstable.

If the fracture data is characterized by the type of fracture, also shown in Figure 3.23, then the data follow the same trend as seen by Kinloch with the data showing a transition between fracture types as the testing temperature approaches T_g [45]. In the broader transition samples, B390 (D230) and B440 (D230), this transition is shifted to closer to T_g as the samples still show stick-slip behavior whereas the other samples showed unstable behavior. The fracture results are summarized in Table 3.9. Also included in the table are the G_{1c} results calculated either from the area of the load-
The overall fracture trend is similar to those seen elsewhere, but if changes in the individual resins at different temperatures are investigated, additional differences are visible. Using the Holm-Šidák method for multiple comparisons with $P < 0.05$ for significance, each pairing within each resin type was compared. SigmaPlot version 12.0 (Systat Software, Inc.) was used to perform this calculation. For D230 the toughness result at $0 \, ^\circ C$ is statistically different than those at 23 and $40 \, ^\circ C$. For D400 and B270 the results at the highest tested temperature, 23 and $40 \, ^\circ C$ respectively, are statistically different than the lower two temperatures. For B440 there is no statistical dependence on

<table>
<thead>
<tr>
<th>Resin</th>
<th>Testing T (°C)</th>
<th>T- $T_g$ (°C)</th>
<th>$K_{1c}$ (MPa m$^{1/2}$)</th>
<th>$G_{1c}$ (J/m$^2$) (from area)</th>
<th>$G_{1c}$ (J/m$^2$) (from $K_{1c}$)</th>
<th>Facture Behavior</th>
</tr>
</thead>
<tbody>
<tr>
<td>D230</td>
<td>0</td>
<td>-92</td>
<td>0.57 ± 0.06</td>
<td>130 ± 60</td>
<td>110 ± 20</td>
<td>S</td>
</tr>
<tr>
<td></td>
<td>23</td>
<td>-69</td>
<td>0.80 ± 0.12</td>
<td>210 ± 60</td>
<td>220 ± 60</td>
<td>S-U-SS</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>-52</td>
<td>0.88 ± 0.11</td>
<td>330 ± 90</td>
<td>280 ± 80</td>
<td>U</td>
</tr>
<tr>
<td></td>
<td>-20</td>
<td>-74</td>
<td>0.79 ± 0.07</td>
<td>260 ± 40</td>
<td>200 ± 30</td>
<td>S</td>
</tr>
<tr>
<td>D400</td>
<td>0</td>
<td>-54</td>
<td>0.82 ± 0.08</td>
<td>250 ± 50</td>
<td>210 ± 40</td>
<td>S</td>
</tr>
<tr>
<td></td>
<td>23</td>
<td>-31</td>
<td>1.31 ± 0.19</td>
<td>750 ± 250</td>
<td>590 ± 180</td>
<td>U</td>
</tr>
<tr>
<td>B270 (D230)</td>
<td>0</td>
<td>-85</td>
<td>0.61 ± 0.06</td>
<td>130 ± 70</td>
<td>120 ± 20</td>
<td>S</td>
</tr>
<tr>
<td></td>
<td>23</td>
<td>-62</td>
<td>0.61 ± 0.10</td>
<td>170 ± 50</td>
<td>130 ± 40</td>
<td>U-SS</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>-45</td>
<td>1.51 ± 0.12</td>
<td>930 ± 180</td>
<td>840 ± 130</td>
<td>U</td>
</tr>
<tr>
<td>B390 (D230)</td>
<td>-20</td>
<td>-82</td>
<td>0.91 ± 0.08</td>
<td>280 ± 50</td>
<td>230 ± 40</td>
<td>S-U</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>-62</td>
<td>1.04 ± 0.11</td>
<td>430 ± 30</td>
<td>370 ± 80</td>
<td>S-U</td>
</tr>
<tr>
<td></td>
<td>23</td>
<td>-39</td>
<td>0.85 ± 0.06</td>
<td>310 ± 60</td>
<td>280 ± 40</td>
<td>U-SS</td>
</tr>
<tr>
<td>B440 (D230)</td>
<td>-20</td>
<td>-76</td>
<td>1.03 ± 0.05</td>
<td>410 ± 70</td>
<td>310 ± 30</td>
<td>S-U</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>-56</td>
<td>0.99 ± 0.03</td>
<td>410 ± 70</td>
<td>360 ± 30</td>
<td>U-SS</td>
</tr>
<tr>
<td></td>
<td>23</td>
<td>-33</td>
<td>0.98 ± 0.07</td>
<td>490 ± 110</td>
<td>450 ± 60</td>
<td>U-SS</td>
</tr>
</tbody>
</table>

*S = Brittle-Stable  
U-SS = Unstable Stick-Slip  
U = Unstable
the testing temperatures. For B390 the middle test temperature, 0 °C, is statistically different from the other two.

Over 40 °C, the two blends with high network heterogeneity, B440 and B390, are less dependent upon temperature than the more homogeneous resins. The B440 is completely insensitive, while B390 is insensitive at the extremes. The slight increase at 0 °C for B390 may be related to the transition from U-S to U-SS. For the other resins, there is a statistically significant increase in toughness with increasing temperature, or conversely, a decrease with decreasing temperature. From an applications point of view, a significant decrease in toughness with decreasing temperature could limit the effective usable temperature range of an item. Temperature insensitive toughness would be beneficial to widen the working temperature range.

3.4 Conclusions

Resins were formed by reacting DGEBA with either monodisperse or bimodal blends of polyether amines. No residual epoxy or amines were seen via FTIR and DSC suggests complete reaction. The reactivity between primary and secondary amines was the same for D400 and B440, the blended amine with similar AHEW, suggesting no changes in the network formation. The bimodal blends matched the T_g and cross-link density of the resins formed using a single, equivalent molecular weight amine. In the rubbery regions, the density of the blends decreased with increasing amine molecular weight. In the glassy regions, blends containing any amount of D230 approached a similar value, while those containing only D400 or D2000 had consistently lower densities. The glassy modulus of the bimodal amine blends can be greater than those of
similar single amine resins, with the modulus increasing with increasing amounts of D2000 for a set temperature below \( T_g \). The \( T_g \) was inversely proportional to the volume fraction of amine in the system, while the total damping of the resins was found to be directly proportional. The breath of \( T_g \) was dependent on both the volume fraction of amine as well as the amine size, and hence network heterogeneity. The resins with bimodal amines showed greater breath of glass transition and in some cases surpassed the breadth of either amine individually.

The measured \( M_c \) values of the epoxy-polyetheramine networks show greater deviation from the theory of rubber elasticity than literature values using either aromatic or short linear amines due to the flexibility of the amines and network defects. The deviations increased with increased average amine molecular weight and can be attributed to cyclization of the D2000. The bimodal blends had little influence on the fracture toughness when plotted vs. \( T-T_g \), though the broader \( T_g \) resins shifted the transition from stable to unstable closer to \( T_g \) and decreased the temperature dependence of the toughness results.
List of References


Chapter 4: Epoxy Polydispersity

4.1 Introduction

The previous chapter showed that changes in distributions of polyetheramines reacted with high purity DGEBA can greatly increase the breadth of the glass transition and influence the fracture behavior. The natural continuation of that work is to use a single amine while changing the epoxy distribution. In this chapter the effects of altering the polydispersity of a DGEBA-type epoxy cured with D230 are investigated.

Attempts to achieve increased toughness through the incorporation of higher molecular weight epoxies into blends with lower weight epoxies have produced mixed results. A bimodal blend of low and high molecular weight DGEBA-based vinyl esters resulted in increased the toughness compared to the toughness of a single molecular weight distribution [1]. Bimodal blends of epoxies cured with a single amine led to increased toughness, but the different molecular weights resulted in phase separation [2]. Mirsa, Manson, & Sperling [3] created a range of theoretical molecular weights between cross-links (M_c) values using Epon resins 825 (epoxy equivalent weight, EEW, = 176 g/mol), 828 (190 g/mol), 834 (296 g/mol) and 1001F (500 g/mol) along with blends of 825 and 1004F (998 g/mol). Three of these blends matched the EEWs of Epon 828, Epon 834, and Epon 1001F. All formulations were cured with MDA (4,4′-methylenedianiline). The bimodal blends matching Epon 828 and Epon 1001F had similar glass transition temperatures (T_g)s and rubbery moduli compared to the single
molecular weight epoxy. The blend of 825 and 1004F matching 834 had a glass transition temperature ($T_g$) 15 °C lower but similar glassy and rubbery moduli. The difference was suggested to be due to the longer chain epoxies reacting first, resulting in a microgel with the shorter epoxies reacting later forming an interpenetrating network. Room temperature tensile experiments also showed no dependence on the molecular weight between cross-links ($M_c$) or $M_c$ distribution. This was attributed to restricted motion of the main chains at room temperature, which continued above $T_g$, as shown by creep experiments.

Vakil and Martin investigated yield and fracture behavior of various epoxies, including two bimodal blends, cured with $m$-phenylenediamine [4]. Their blends were mixtures of Epon 825 (EEW=175 g/mol) with Epon 1004F (833 g/mol) matching the EEW of 1001F (545 g/mol) and Epon 825 with Epon 1001F to match Epon 836 (EEW=315 g/mol). They concluded that fracture properties are not sensitive to epoxy molecular weight distributions, although the two blends appear to be only briefly examined.

Haris and co-authors blended Epikote 828 (EEW=190 g/mol) with Epikote 1001 (EEW=475 g/mol) in various proportions from pure 828 to pure 1001 [5-6]. The blends were cured with an anhydride curing agent. The temperature of maximum tan $\delta$ was decreased from either epoxy for all blends, while the fracture toughness steadily increased with increasing amount of 1001, the higher molecular weight epoxy.

These previous studies with blends of various molecular weight epoxies only used aromatic or anhydride curing agents [3-6], so there was little flexibility in the resulting networks; any influence the epoxy distribution had could have easily been masked. In
addition, few of the prior studies had a comparable single distribution epoxy for reference. In this chapter high purity DGEBA is blended, individually, with several higher molecular weight epoxies to match the EEW of a semi-solid DGEBA epoxy (n~0.5) and any effects on thermal and mechanical properties investigated.

Figure 4.1: Structure of A) DGEBA and B) D230, n ~ 2.5

4.2 Experimental

4.2.1 Blend Formation

Seven Epon epoxies with molecular weights ranging from 352 g/mol to over 5000 g/mol were obtained from Momentive and their characteristics are listed in Table 4.1. All of the 1000 series resins are solid at room temperature. Epon 825 and 834 are liquids, but 834 has a much higher viscosity. The epoxies’ EEWs were taken from the manufacturer’s certificates of analysis and confirmed following ASTM D 1652-90 Test Method B [7]. Epon 834 with an EEW of 246 g/mol was chosen as the basis of comparison. The blend ratios are given in Table 4.2. To create the blends, appropriate amounts of 825 and a solid epoxy were heated in a glass jar and periodically stirred until
the solid epoxy melted and a homogeneous mixture was obtained. Blends containing 1001F, 1002F, and 1004F were heated to 125 °C while the blends containing 1007F and 1009F were heated to 150 °C. The epoxy blends were degassed while warm to remove any volatiles or entrapped air. The resulting blends were clear, tacky semi-solids at room temperature. The EEWs of the blends were also tested and were confirmed to match the EEW (±1) of Epon 834.

Table 4.1: Epoxy equivalent weights and values of n.

<table>
<thead>
<tr>
<th>Resin</th>
<th>Epoxy Equivalent Weight (EEW) (g/mol)</th>
<th>Average n</th>
</tr>
</thead>
<tbody>
<tr>
<td>Epon 825</td>
<td>176</td>
<td>0.04</td>
</tr>
<tr>
<td>Epon 834</td>
<td>246</td>
<td>0.54</td>
</tr>
<tr>
<td>Epon 1001F</td>
<td>528</td>
<td>2.52</td>
</tr>
<tr>
<td>Epon 1002F</td>
<td>663</td>
<td>3.47</td>
</tr>
<tr>
<td>Epon 1004F</td>
<td>853</td>
<td>4.81</td>
</tr>
<tr>
<td>Epon 1007F</td>
<td>1810</td>
<td>11.55</td>
</tr>
<tr>
<td>Epon 1009F</td>
<td>2774</td>
<td>18.34</td>
</tr>
</tbody>
</table>

Table 4.2: Ratio of components in blends matching 834’s EEW.

<table>
<thead>
<tr>
<th>Resin</th>
<th>Weight % 825</th>
<th>Mole % 825</th>
</tr>
</thead>
<tbody>
<tr>
<td>825/1001F</td>
<td>57.3</td>
<td>80.1</td>
</tr>
<tr>
<td>825/1002F</td>
<td>61.3</td>
<td>85.6</td>
</tr>
<tr>
<td>825/1004F</td>
<td>64.1</td>
<td>89.7</td>
</tr>
<tr>
<td>825/1007F</td>
<td>68.5</td>
<td>95.7</td>
</tr>
<tr>
<td>825/1009F</td>
<td>69.6</td>
<td>97.3</td>
</tr>
</tbody>
</table>
4.2.2 Polydispersity

Twice the EEW is equivalent to the number-average molecular weight assuming ideal structures; however it does not give any information on the weight-average molecular weight or polydispersity. Gel permeation chromatography (GPC) was performed to quantify the polydispersity of the as-received epoxies as well as the blends. A Waters 515 GPC was used with two 30 cm long, 7.5 mm diameter, 5 µm styrene-divinyl benzene columns in series. The columns were equilibrated and run at 45 °C using tetrahydrofuran (THF, Sigma-Aldrich, 99.9%) as the elution solvent at a flow rate of 1 mL/minute. The column effluent was monitored by two detectors operating at 25 °C: a Waters 2410 refractive index (RI) detector and a Waters 2487 dual absorbance detector operating at 270 and 254 nm. Samples had concentrations of 1-2 mg epoxy per mL THF. Data from the RI detector was used for polydispersity analysis. The molecular weight calibration curve was based upon polystyrene standards for the higher molecular weights, and the discrete peaks for DGEBA with n=0, 1, and 2 for the low molecular weights.

4.2.3 Resin Cure

The epoxy was heated to 80-85 °C and a stoichiometric amount of Jeffamine D230 (Huntsman), a linear polyether diamine whose structure is shown in Figure 4.1B, was added, with two epoxy groups per amine. The resin was thoroughly mixed by hand and then mixed and defoamed using an ARE-250 centrifugal mixer (Thinky Corp.) before being poured into silicone rubber molds (preheated to 80 °C) and cured for 2 h at 80 °C. The samples were removed from the mold and post cured for 2 h at 125 °C. All cured samples were transparent indicating that macrophase separation did not occur.
4.2.4 Polymer Characterization

Near-infrared (NIR) spectroscopy was used to investigate the extent of cure. In the NIR region, epoxide groups show peaks at 4530 and 6060 cm$^{-1}$; primary amines have a peak at 4925 cm$^{-1}$ while a peak at 6534 cm$^{-1}$ is caused by primary and secondary amines[8]. Spectra of the neat monomers and the cured samples were taken using a Nicolet Nexus 870 infrared spectrometer. The spectra of the cured samples were qualitatively examined for residual epoxy or amine functionality.

Samples with approximate dimensions of 35 × 12 × 3.25 mm$^3$ were tested on a TA Instruments Q800 Dynamic Mechanical Analyzer using the single cantilever clamp, operating at 1 Hz with 7.5 μm displacement. Samples were allowed to equilibrate at 0 °C for 10 minutes before increasing the temperature by 2 °C/minute to 200 °C.

The temperature at which the peak in the loss modulus occurred was considered the $T_g$ of the resin [9]. All samples had a definite point in the loss modulus where the rubbery modulus began to increase with increasing temperature; this point was used to calculate the molecular weight between cross-links, $M_c$. The theory of rubber elasticity was used to calculate the $M_c$, equation 4.1, from dynamic mechanical analysis (DMA) data:

$$M_c = \frac{3RT\rho}{E'}$$  \hspace{1cm} 4.1

where $R$ is the universal gas constant, $T$ the absolute temperature, $\rho$ the density, and $E'$ the modulus of the rubbery plateau. Rubber elasticity applies to polymers with low cross-link densities and may not give completely accurate cross-link density measurements for highly cross-linked epoxies [10]. Nonetheless, numerous researchers
have used it as a measure of cross-link density, and it seems to show good trends for sample sets with similar chemistries [11-12].

The densities of all samples were measured using the water displacement method outlined in ASTM Standard D792–00 [13]. Density measurements were made using the broken pieces from the fracture tests, described in the following paragraph. The coefficients of thermal expansion, CTE or α, in both the rubbery and glassy regions were measured using a TA Instruments Q400 Thermomechanical analyzer. Samples for thermomechanical analysis (TMA) were made by cutting the fracture compliance samples into pieces approximately 5 × 5 × 12.7 mm³. A constant force of 0.05 N was used for both the preload and the applied load. Samples were heated from room temperature to 125 °C, cooled to -70 °C, then heated to 150 °C at 3 °C/min. The initial heating cycle was to remove any residual stress. The CTE values from the final cycle, -70 to 150 °C, were used to calculate the density as a function of temperature assuming isotropic behavior. Four samples per resin were tested for density measurements and two to three samples per resin for CTE measurements.

Fracture toughness, $K_{1c}$, was measured using the compact tension geometry according to ASTM D5045 [14]. Samples were cured in silicone rubber molds with nominal dimensions of 30.5 × 32 × 12.7 mm³. A 10 mm long notch was cut into each sample with a diamond saw. The samples and single edged razors were placed in a freezer overnight (approximately -20 °C) to ensure all samples were well within their glassy region when starter cracks were made. Samples and razor blades were removed from the freezer; the razor was inserted into the notch and tapped with a hammer, until a crack propagated approximately 9 mm into the sample, leaving a ligament of
approximately 13 mm for the crack to propagate through during testing. These cracks were of the “instantly propagated” type, shown by Ma et al. to give minimum $K_{1c}$ values [15]. Seven samples per resin were tested at room temperature. After fracture, the unmodified fracture surfaces were imaged using an Olympus MX50 optical microscope.

4.3 Results & Discussion

4.3.1 GPC Results

The Epon 1000 series of epoxies used in this work are reported to be fusion grade epoxies, meaning predominately even numbers of repeat units were expected. However, depending on the batch used, the molecular weight (MW) distribution of the epoxy can vary. Previous work showed that a batch of Epon 1004F manufactured prior to 2004 had components up to $n=6$-$8$ and a PDI of 1.3 [1]. A more recent batch, manufactured in 2008 and used in this work, contained monomers with $n=0$, small quantities of $n=1$ and $n=2$, then the maximum matching $n=14$, as shown in Figure 4.2, with a PDI of 2.82. Although the PDIs were very different for these batches, the EEWs were similar, 900 and 853, respectively. Misra et al. identified the components of their blends [3], which included Epon 1004F with a major component of $n=12$, but did not quantify the PDI. Vakil and Martin did not consider molecular weight distributions of their epoxies [4].
Figure 4.2 shows the processed GPC spectra of the higher molecular weight epoxies. In all cases, the most intense peak comes from high molecular weight epoxies ($n \geq 12$). Though in the 1001F, 1002F, and 1004F there are significant peaks representing DGEBA with $n = 0$, 1, or 2. Figure 4.3 shows the GPC spectra of the blends, along with that of 834. For all the blends, the peak for pure DGEBA ($n = 0$) is the strongest, though in 834’s case, the $n=4$ peak is also very strong. With the shift of the other peaks to shorter elution times (higher molecular weights), the PDI of the blends increased. Even though the blends are only composed of two epoxies, the broad distributions disqualify
them from being termed “bimodal” as Vakil did, while instead “polydisperse” better represents these epoxy blends.

Figure 4.3: GPC spectra of blends and 834, normalized to their most intense peak (n=0). All resins have equivalent EEWs and are shifted vertically for clarity.

Number and weight average molecular weights (M_n and M_w, respectively) were calculated from the GPC results. Igor Pro (WaveMetrics Inc.) was used to remove noise and flatten the baseline. The weight fraction eluted at time i, w_i, was calculated by equation 4.2:
\[ w_i = \frac{I_i}{\sum_i I_i} \quad 4.2 \]

where \( I_i \) is the intensity of the spectrum at time \( i \). Using \( w_i \), the number and weight average molecular weights were calculated according to equations 4.3 and 4.4, and the polydispersity index (PDI) by \( M_w/M_n \).

\[ M_n = \sum \frac{M_i}{w_i} \quad 4.3 \]

\[ M_w = \sum w_i M_i \quad 4.4 \]

The molecular weight eluted at a given time (\( M_i \)) was determined from the calibration curve. Table 4.3 shows the calculated molecular weights of the individual epoxies and blends along with their PDIs.

The \( M_n \) calculated from the GPC results did not match the epoxy titration results for several reasons. The calibration curve was a best fit line between the elution times of known molecular weights, resulting in some mismatch. Also, the calculation of \( w_i \) assumes a continuous molecular weight distribution. Ideally the distribution should be discrete weights separated by multiples of 284 g/mol, the value of the repeat unit in Figure 4.1A. While the ideal structure may be present for the lower molecular weight epoxies, the ideal difunctional form is not always present in higher molecular weights as shown by Julka et al. who tentatively identified nine types of non-ideal species, with one to three epoxy groups in solid epoxies [16]. These combine to result in the mismatch between the titration and GPC results. These results could indicate that Epon epoxies are not fully epoxidized; however, past results have confirmed agreement between epoxy
titration and nuclear magnetic resonance spectroscopy with slight differences from the SEC results [1]. These results showed that the epoxies contain a very high fraction of diepoxidized monomers and no significant fraction of mono-functional epoxies and non-epoxidized bisphenol A [1].

Table 4.3: $M_n$ from epoxy titrations and GPC data along with PDI of epoxy resins and blends.

<table>
<thead>
<tr>
<th>Individual Epoxies</th>
<th>$M_n$ (g/mol) (2x EEW)</th>
<th>$M_n$ (g/mol) (GPC)</th>
<th>PDI (GPC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>825</td>
<td>352</td>
<td>365</td>
<td>1.06</td>
</tr>
<tr>
<td>834</td>
<td>492</td>
<td>557</td>
<td>1.81</td>
</tr>
<tr>
<td>1001F</td>
<td>1056</td>
<td>1331</td>
<td>2.22</td>
</tr>
<tr>
<td>1002F</td>
<td>1326</td>
<td>1648</td>
<td>2.34</td>
</tr>
<tr>
<td>1004F</td>
<td>1706</td>
<td>2069</td>
<td>2.82</td>
</tr>
<tr>
<td>1007F</td>
<td>3620</td>
<td>3284</td>
<td>3.82</td>
</tr>
<tr>
<td>1009F</td>
<td>5548</td>
<td>4256</td>
<td>3.62</td>
</tr>
<tr>
<td>Blends</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>825-1001F</td>
<td>492</td>
<td>546</td>
<td>2.98</td>
</tr>
<tr>
<td>825-1002F</td>
<td>492</td>
<td>566</td>
<td>3.68</td>
</tr>
<tr>
<td>825-1004F</td>
<td>492</td>
<td>550</td>
<td>4.83</td>
</tr>
<tr>
<td>825-1007F</td>
<td>492</td>
<td>542</td>
<td>9.50</td>
</tr>
<tr>
<td>825-1009F</td>
<td>492</td>
<td>522</td>
<td>10.71</td>
</tr>
</tbody>
</table>

4.3.2 Extent of Cure

After cure, no trace of the amine peaks at 4925 cm$^{-1}$ and 6534 cm$^{-1}$ was observed, as shown in Figure 4.4. The epoxide peak at 4530 cm$^{-1}$ had also completely vanished. It was less clear if there was a residual epoxide peak at 6066 cm$^{-1}$ because that peak overlaps with the aromatic peak at 5960 cm$^{-1}$ and must be deconvoluted for analysis [8].
The 4530 cm⁻¹ peak provides a direct means of monitoring epoxy concentration [17] and the absence of it and the amine peaks confirmed complete reaction.

Figure 4.4: FTIR spectra of neat components and cured 834-D230. Inset shows the epoxide peak at 4530 cm⁻¹.

4.3.3 DMA Results

The DMA results showed very little difference among the blends (Table 4.4). The 30 °C storage moduli were 2.2–2.3 GPa and the T₆₅s ranged from 97.0 – 98.5 °C. Using the full width at half max (FWHM) of the tan δ curve as the breadth of the glass transition, there was still no change as the PDI of the epoxies increased. This is contrary
to the behavior seen when the distribution of linear amines was increased; in those cases the breadth of transition greatly increased and the modulus at 30 °C decreased [18]. The temperature at which the minimum in the storage modulus occurred did increase for 825-1007F and 825-1009F but those samples also showed the greatest variation in those temperatures. The moduli values of those minima were similar to the other resins. Using those minimum rubbery modulus values and density at those temperatures (extrapolated from room temperature measurements using TMA data as discussed in the next section), \( M_c \) values for the resins were calculated. Figure 4.5 shows the \( M_c \) values and \( T_g \)'s versus the PDI of the epoxies. Within error, there is no trend between \( M_c \) or \( T_g \) with increasing polydispersity; however, \( M_c \) and \( T_g \) do show the typical inverse correlation.
Figure 4.5: $M_c$ and $T_g$ versus epoxy polydispersity.

<table>
<thead>
<tr>
<th>Resin</th>
<th>$30^\circ$ C Storage Modulus (MPa)</th>
<th>$T_g$ (°C)</th>
<th>$T_g$ breadth (°C)</th>
<th>Tan $\delta$ max (°C)</th>
<th>Min. Storage Modulus (MPa)</th>
<th>Temp. at Min. Modulus (°C)</th>
<th>Density at 23 °C (g/cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>834</td>
<td>2310 ± 80</td>
<td>97.0 ± 1.7</td>
<td>10.8 ± 1.2</td>
<td>102.3 ± 1.1</td>
<td>15.7 ± 0.4</td>
<td>124.4 ± 2.3</td>
<td>1.1613 ± 0.0005</td>
</tr>
<tr>
<td>825-1001</td>
<td>2290 ± 90</td>
<td>97.5 ± 1.7</td>
<td>10.5 ± 0.7</td>
<td>102.8 ± 1.0</td>
<td>15.3 ± 0.8</td>
<td>125.1 ± 0.7</td>
<td>1.1603 ± 0.0002</td>
</tr>
<tr>
<td>825-1002</td>
<td>2300 ± 50</td>
<td>98.5 ± 0.9</td>
<td>10.1 ± 0.3</td>
<td>103.5 ± 0.6</td>
<td>16.5 ± 0.5</td>
<td>124.9 ± 2.8</td>
<td>1.1597 ± 0.0004</td>
</tr>
<tr>
<td>825-1004</td>
<td>2230 ± 10</td>
<td>98.5 ± 0.7</td>
<td>10.0 ± 0.4</td>
<td>103.5 ± 0.7</td>
<td>16.5 ± 0.2</td>
<td>124.6 ± 2.3</td>
<td>1.1597 ± 0.0005</td>
</tr>
<tr>
<td>825-1007</td>
<td>2340 ± 50</td>
<td>96.8 ± 2.3</td>
<td>10.5 ± 0.8</td>
<td>102.1 ± 2.1</td>
<td>15.1 ± 0.6</td>
<td>138.8 ± 5.1</td>
<td>1.1599 ± 0.0006</td>
</tr>
<tr>
<td>825-1009</td>
<td>2370 ± 40</td>
<td>97.6 ± 1.3</td>
<td>10.3 ± 0.7</td>
<td>102.8 ± 1.0</td>
<td>15.4 ± 0.5</td>
<td>136.8 ± 7.3</td>
<td>1.1604 ± 0.0005</td>
</tr>
</tbody>
</table>
4.3.4 Density & CTE

All samples had very similar room temperature densities, with the slight variations following no pattern. Also, all samples had similar CTE behavior, shown in Figure 4.6. While a constant or mean value for glassy CTE is often reported [19-22], CTEs for epoxies are temperature dependent [23-24]. Here from -50 °C to 40 °C the CTEs changed from approximately 60 \( \mu \text{m} \cdot \text{m}^{-1} \cdot \text{°C}^{-1} \) to over 80 \( \mu \text{m} \cdot \text{m}^{-1} \cdot \text{°C}^{-1} \). For comparison over a similar temperature range, pure aluminum’s CTE changes by only 1.6 \( \mu \text{m} \cdot \text{m}^{-1} \cdot \text{°C}^{-1} \) [25]. The slopes of the CTEs in the glassy region were calculated by averaging the best-fit linear curves from -50 °C to 40 °C, with the results shown in Figure 4.7. All linear fits had \( R^2 \) values greater than 0.99 except for one sample of 825-1009F \( (R^2=0.987) \). A trend appears in these slopes, with the slope decreasing with increasing epoxy PDI. This declining rate of change in CTE could be a result of the increased softening point of the higher molecular weight epoxies. The increasing number of secondary hydroxyl groups with increasing molecular weight increase the softening points of the solid epoxies due to hydrogen bonding; 1007 and 1009 have softening points of 125 °C and 135 °C, respectively [26]. While the blends should have similar amounts of hydroxyl groups and bonds, the distribution of hydroxyls was altered, possibly allowing for better hydrogen bond alignment, resulting in decreased rate of change in CTE.

Above the \( T_g \), the CTEs drop slightly and could be indicative of rubber elasticity contraction of the samples [10]; however, this may be an artifact due to the compression
of the then-rubbery samples. Elsewhere CTEs of epoxies above the $T_g$ are shown to be slightly increasing when measured using a lower applied force [27].

Figure 4.6: CTE curves, shifted vertically for clarity. Error bars are most noticeable in the transition region, but are present throughout, except below 0 °C, where they were removed to enhance distinction between the curves.
Figure 4.7: Slope of the glassy CTE (-50-40 °C).

By assuming isotropic expansion, the CTE measurements were used to transform the measured room temperature densities into a function of temperature. The resulting curves are shown in Figure 4.8. The glassy densities of the resins followed the same pattern as observed at room temperature while above the $T_g$s the densities collapse onto one curve.
Figure 4.8: Density as a function of temperature; the dotted line indicates the maximum in CTE values. Inset shows that the room temperature differences extend through the glassy region.

The measured densities and maximum CTE values follow the same trend, with 834 having the highest values, 825-1002F and 825-1004F having the lowest values, and the value increase again for 825-1007F and 825-1009F, as shown in Figure 4.9. In the rubbery regime, the densities converge to the same value. This is contrary to our previous work where the densities diverged in the rubbery regime [18]. The diverging densities were seen in formulations with varying amine molecular weights and amounts, whereas the converging densities seen here had formulations with the same amount of a single molecular weight amine. These suggest that the amine controls the ultimate expansion as the polyether chains are more flexible than the aromatic epoxy. This
density convergence begins before the questionable rubbery CTE region and therefore is not suspect. In the glassy regime, the differences in density may be due to packing differences caused by structural differences in the higher molecular weight epoxies. As mentioned above, non-ideal structures can be found in solid epoxies, it is possible that more non-ideal structures were present in the 1002 and 1004 resins than the others, leading to poorer packing and lower glassy densities.

Figure 4.9: Maximum CTE and measured (at 23 °C) densities of resins.
As the CTEs and densities of the resins are, in general, similar, it is insightful to compare those properties to other related systems. Figure 4.10 shows the CTEs of 834-D230 along with 825 cured with D230 and two other molecular weights of the polyetheramine, D400 and D2000. In addition, 825 cured with a blend of D230 and D2000 with an average molecular weight equivalent to D400 (here termed B440) is also shown. The experimental details of these other resins are described elsewhere [18].
Compared to the 825 resins, 834 and the more polydisperse epoxies have slightly higher glassy CTEs. Above $T_g$, the CTEs are similar to the 825-D230, but lower than 825-D400, 825-B440, and 825-D2000, again suggesting that the more flexible amine controls the high temperature expansion. For the transition region from glassy to rubbery, the 834 shows a broader transition, 34 °C, than the 825 with single amines, 25, 19, and 25 °C for D230, D400, and D2000 respectively, but much less than the resin with blended amines, 825-B440, 43°C. Increasing the epoxy polydispersity from 1.81 to 10.71 does not change this transition region, whereas changing it from 1.06 to 1.81 and decreasing the EEW does (comparing Epon 825 to Epon 834). Despite this broader transition region as measured by TMA, the DMA breadth of $T_g$ for the polydisperse epoxies are very similar compared to high purity DGEBA cured with D230 [18].

### 4.3.5 Fracture Toughness

As with the DMA results, the fracture toughness results also presented a null change, shown in Figure 4.11. Although 825-1001F, 825-1002F, 825-1004F, and 825-1007F appear to have slightly higher fracture properties than 834 and 825-1009F, the toughness values were similar within the error of the tests. $G_{1c}$ was similar whether calculated from $K_{1c}$ using the DMA modulus or from the area under the load displacement curve. Given these results, it is possible that resins with a high weight percentage of higher molecular weight component, as in the 825-1001F blend have high toughness and as the weight percent of higher molecular weight component decreased, the toughness decreased to a minimum of that of the 834 and the 825-1009F samples. However, given the error in the result, it is not possible to make this conclusion.
Furthermore, in a similar experiment using bimodal amines, we measured significant increases in fracture toughness for blends relative to non-blended samples and changes in fracture behavior, showing that changing the amine polydispersity has a much more pronounced effect on fracture toughness than epoxy polydispersity. Here, all samples showed unstable stick-slip crack propagation, as has been seen elsewhere for unmodified epoxies [28]. In comparison, when the amine is blended, the fracture behavior changed compared to the single amine counterpart - from unstable for the single amine to slip-stick at room temperature and from brittle-stable to stable-unstable slip-stick at -20 °C [18]. The -20 °C results may be more relevant when the amine is blended as -20 °C is approximately 75 °C below those resins’ T_g, whereas room temperature is approximately 75 °C below the polydisperse epoxies’ T_g. It appears that changing the amine’s dispersity slightly blunted the growing crack while changing the dispersity of the stiff epoxy has no effect on crack growth.
The fracture surfaces of all samples were very smooth. Figure 4.12 is an optical microscopy image of the bulk surface. The surfaces had no visible differences between the low PDI and high PDI samples. Crack propagation is right-to-left in all images. The lack of degassing did result in some entrapped air in the samples that were visible during microscopy analysis; however they were few (0-2 per samples) and unlikely to affect the toughness. Air bubbles were not observed in the smaller DMA samples.
4.4 Conclusions

Epoxy blends were formulated that had large DGEBA molecular weight distributions, with PDIs ranging from 3 to over 10 while maintaining equivalent EEWs. When cured with a polyetherdiamine, the resins had similar $T_g$s, moduli, $M_c$ values, densities, and fracture properties. Slight differences were seen in the slope of the glassy CTE with the slope decreasing with increasing epoxy polydispersity. Despite these differences, the rubbery densities collapsed onto a single curve. The polydisperse epoxies did show broadening in the CTE transition region although narrower relative to bimodal amine blends; however, any epoxy polydispersity caused this broadening to appear. All resins exhibited the same slip-stick fracture behavior. These results corroborate the molecular weight distribution independence concluded from previous work with polydisperse epoxies cured with aromatic amines. This is in contrast to the distribution dependency seen for polydisperse linear amines cured with a single...
molecular weight epoxy, where $T_g$, breadth of $T_g$, and fracture toughness increased as a result of blending. Thus, the conclusion is that epoxy resins are far more sensitive to distributions in the flexible portion, rather than the more rigid one.


Chapter 5: Alternate Structures

5.1 Introduction

Chapter 3 compared resins containing a single rigid epoxy with a blend of flexible amines while Chapter 4 compared blends of rigid epoxies with a single flexible amine. This chapter expands on structural changes to the polymer networks, specifically the addition of flexibility to the epoxy.

The DGEBA and DGEBA-based epoxies used previously gain stiffness by having two methyl groups coming off the central carbon between the two phenol rings. If those methyl groups are not present, as in diglycidyl either of bisphenol F (DGEBF), the phenol rings are less restricted, leading to increased chain flexibility. In addition DGEBF is a mixture of isomers with the glycidyl chain ortho or para to the center linkage; this reduces the crystallinity, which is often experienced with DGEBA, and possibly the packing of the cured polymer. DGEBF is actually the lowest molecular weight species of the multi-functional phenol novolac epoxies but with the $n$ of the repeat unit typically being <0.2, shown in Figure 5.1A. It has slightly higher functionality than DGEBA but lower viscosity [1]. Replacing the DGEBA with DGEBF is the first structural change investigated in this chapter.
The other structural change to be investigated in this chapter is the opposite network structure of what was used in other chapters: a linear epoxy with rigid amines. The polyether amines used previously have a poly(propylene glycol) (PPG) backbone. Poly(propylene glycol) diglycidyl ethers (PPGGE), Figure 5.1B, in different molecular weights are available to provide the epoxy analogs to the D230 and D400 amines. An epoxy analog of D2000 is not commercially available and efforts to synthesis one inhouse did not result in complete epoxidation. Instead diglycidyl ether of poly(ethylene glycol) (PEGGE), Figure 5.1C, is used as its backbone is similar. Lower molecular weight PEGGEs were not available with close to two epoxies per molecule. The linear epoxies are cured with several different amines.

5.2 Experimental

5.2.1 Materials

DGEBF was obtained from Momentive under the name Epon 862 with an EEW of 170 g/mol and $n = 0.17$. DGEBA, Epon 825, with EEW = 175 and $n = 0.04$, was also
obtained from Momentive. PPGGE with approximate molecular weights of 380 and 640 g/mol were obtained from Sigma-Aldrich. PEGGE with approximate molecular weight of 2000 was also obtained from Sigma-Aldrich. PEGGE2000 is a crystalline solid, with a melting point around 50 °C. Only the DGEBF, DGEBA, and PPGGE-640 were supplied with manufacturer’s data regarding the EEW. These EEWs were verified following ASTM D1652 [2] and the same procedure was used to measure the EEWs of the other epoxies.

![Figure 5.2: Structure of A) 4,4’-methylenedianiline (MDA), B) 4,4’-methylenebiscyclohexanamine (PACM), C) 2,2’-dimethyl-4,4’-methylenebis(cyclohexylamine) (MPACM) and D) 1,3 phenylenediamine (PDA).]

Of available amines, 4,4’-methylenedianiline (MDA), shown in Figure 5.2A, would be an ideal amine analogue for DGEBF for use with the linear amines; however, MDA is a known carcinogen and toxin [3]. An alternative, 4,4’-methylenebiscyclohexanamine (PACM), shown in Figure 5.2B, from Air Products, is instead used. Another amine is 2,2’-dimethyl-4,4’-methylenebis(cyclohexylamine), commercially available as Ancamine® 2049, Figure 5.2C, is similar to PACM with the addition of two methyl groups and henceforth will be referred to as MPACM; it is also from Air Products. 1,3 phenylenediamine (PDA), Figure 5.2D, from Sigma-Aldrich was
also used; the meta phenylenediamine was chosen over the para configuration due to reduced health hazards. Additionally the Jeffamines and some of the Jeffamine blends described in previous chapters are also used.

5.2.2 GPC

The amines used here, other than D230, are reported to have purities of 99+\% by their manufacturers. The epoxies are distributions of molecular weights. Gel permeation chromatography (GPC) was performed to quantify the polydispersity of the PPG-based epoxies; the polydispersity of the PEGGE is supplied by the manufacturer and the known \( n \) of the DGEBF gives an idea of its polydispersity. A Waters 515 GPC was used with two 30 cm long, 7.5 mm diameter, 5 µm styrene-divinyl benzene columns in series. The columns were equilibrated and run at 45 °C using tetrahydrofuran (THF, Sigma-Aldrich, 99.9\%) as the elution solvent at a flow rate of 1 mL/minute. The column effluent was monitored by a Waters 2410 refractive index (RI) detector. Samples had concentrations of 1-2 mg epoxy per mL THF. The molecular weight calibration curve was based upon polystyrene standards for the higher molecular weights, and the discrete peaks for DGEBA with \( n = 0, 1, \) and 2 for the low molecular weights.

5.2.3 Resin Cure and Characterization

DGEBF is cured with several of the amine and amine blends from Chapter 3: D230, D400, B270, and B440. In addition it was cured with PACM. Table 5.1 shows the mix ratios and the cure conditions for those resins. The comparable DGEBA-based resins from previous chapters are used for comparison.
For the linear epoxies, PPGGE640 was cured with PDA, PACM, MPACM, and D230 while the PPGGE380 was cured with PACM and D230. PEGGE2000 was only cured with PACM. Additionally a blend of PPGGE380 and PEGGE2000 was made to match the EEW of PPGGE640; this blend was also cured with PACM. Table 5.2 shows the mix ratios and cure conditions for all these resins. MPACM has more steric hindrance than PACM and a longer and higher temperature cure cycle was used [4]. In general, the linear amines are slower reacting, hence the longer cure times compared to the DGEBF resins. The PDA was cured following the cycle outlined in Chapter 2. The extent of cure for the linear epoxies was also qualitatively assessed using NIR as described in Chapter 3. Additionally samples made containing PEGGE2000 were analyzed with DSC with a heat/cool/heat cycle over a temperature range of -90 – 100 °C at 10 °C/min for determination of residual crystallinity and examine any residual exotherm.

<table>
<thead>
<tr>
<th>Resin</th>
<th>Mix Ratio</th>
<th>Cure Schedule</th>
</tr>
</thead>
<tbody>
<tr>
<td>DGEBF/PACM</td>
<td>100/30.1</td>
<td>2 h at 80 °C + 2 h at 160 °C</td>
</tr>
<tr>
<td>DGEBF/D230</td>
<td>100/35.5</td>
<td>2 h at 80 °C + 2 h at 125 °C</td>
</tr>
<tr>
<td>DGEBF/B270</td>
<td>100/35.0/4.8</td>
<td>2 h at 80 °C + 2 h at 125 °C</td>
</tr>
<tr>
<td>DGEBF/D400</td>
<td>100/65.4</td>
<td>2 h at 80 °C + 2 h at 125 °C</td>
</tr>
<tr>
<td>DGEBF/B440</td>
<td>100/31.4/34.0</td>
<td>2 h at 80 °C + 2 h at 125 °C</td>
</tr>
</tbody>
</table>
Table 5.2: Mix ratios and cure schedule of linear epoxies.

<table>
<thead>
<tr>
<th>Resin</th>
<th>Mix Ratio Epoxy/Amine (g)</th>
<th>Cure Schedule</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPGGE380/PACM</td>
<td>100/28.3</td>
<td>4 h at 100 °C + 4 h at 125 °C + 2 h at 160 °C</td>
</tr>
<tr>
<td>PPGGE640/PACM</td>
<td>100/16.2</td>
<td>4 h at 100 °C + 4 h at 125 °C + 2 h at 160 °C</td>
</tr>
<tr>
<td>PPGGE640/MPACM</td>
<td>100/18.5</td>
<td>2 h at 80 °C + 8 h at 150 °C + 2 h at 200 °C</td>
</tr>
<tr>
<td>PPGGE640/PDA</td>
<td>100/8.3</td>
<td>2 h at 80 °C + 2 °C/min to 225 °C + 20 min at 225 °C</td>
</tr>
<tr>
<td>PEG2000/PACM</td>
<td>100/4.9</td>
<td>Preheat to 80 °C, 4 h at 100 °C + 4 h at 125 °C + 2 h at 160 °C</td>
</tr>
<tr>
<td>PPGGE380/PEG2000/PACM</td>
<td>48.0/52.0/16.2</td>
<td>Preheat to 80 °C, 4 h at 100 °C + 4 h at 125 °C + 2 h at 160 °C</td>
</tr>
<tr>
<td>(Average EEW ≈ PPGGE640)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PPGGE380/D230</td>
<td>100/32</td>
<td>4 h at 80 °C + 4 h at 125 °C</td>
</tr>
<tr>
<td>PPGGE640/D230</td>
<td>100/18.2</td>
<td>8 h at 80 °C + 8 h at 125 °C</td>
</tr>
</tbody>
</table>

Blends were also made by replacing some of the epoxy in the PPGGE/PACM resins with 825, as described in Table 5.3. This allowed the total linear portion of the resin to be controlled while maintaining stoichiometry. In addition, blends were made with a targeted $T_g$ similar to the 825-D400 resin used in Chapter 3.
Table 5.3: Mole and mass ratios for 825 blended with PPGGE; cured with the amount of PACM and conditions described in Table 5.2.

<table>
<thead>
<tr>
<th>Mole Ratios (PPGGE/825)</th>
<th>Mass (g) (PPGGE/825)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPPGE380 100/0</td>
<td>100.0/0.0</td>
</tr>
<tr>
<td>PPPGE380 75/25</td>
<td>75.0/23.6</td>
</tr>
<tr>
<td>PPPGE380 50/50</td>
<td>50.0/47.2</td>
</tr>
<tr>
<td>PPPGE380 25/75</td>
<td>25.0/70.8</td>
</tr>
<tr>
<td>PPPGE380 0/100</td>
<td>0.0/94.4</td>
</tr>
<tr>
<td>PPPGE380 65.3/34.7*</td>
<td>65.3/32.8*</td>
</tr>
</tbody>
</table>

| PPGGE640 100/0         | 100.0/0               |
| PPGGE640 90/10         | 90.0/5.4              |
| PPGGE640 80/20         | 80.0/10.8             |
| PPGGE640 75/25         | 75.0/13.5             |
| PPGGE640 50/50         | 50.0/26.9             |
| PPGGE640 35/65         | 35.0/35.0             |
| PPGGE640 25/75         | 25.0/40.4             |
| PPGGE640 0/100         | 0.0/53.8              |
| PPGGE640 36.9/63.1*    | 36.9/34.0*            |

*based on the results of the other blends, these blends were designed to have similar Tg compared to 825-D400

5.2.4 DMA Characterization

All samples were characterized by DMA with a heating rate of 2 °C/min, although the temperature ranged varied depending on the samples’ Tgs. For the samples containing DGEBF samples were tested using the DC and/or SC clamps. All samples contributing to reported moduli had span-to-thickness ratios >10, as determined to give good glassy modulus results in Chapter 2. For resins with linear epoxies, samples with thickness of approximately 3 mm or thicker, for rubbery results, were tested. For the resins with linear epoxies blended with 825, both thin (S-T >10) and thick samples were tested on the SC clamp. Instead of specifying an oscillating amplitude, the oscillation strain was instead set, so that similar strains were applied to samples of different
thicknesses. The strain was set to 0.02%, which is the typical strain experienced by a 3 mm thick sample on either the SC or DC clamp with 7.5 μm oscillating amplitude.

5.2.5 Fracture Toughness

Select resins were also tested for fracture toughness according to ASTM D5045[5] in the SENB geometry. Instantly propagated cracks were initiated at room temperature for DGBF/PACM samples and at -20 °C for other samples. All of the resins containing DGBF except for B270 were tested. For the linear epoxies, only those with $T_g$s targeted to match 825-D400 were tested. The linear epoxies were tested at 0 °C while the others were tested at room temperature.

5.3 Results and Discussion

5.3.1 DGBF Resins: DMA

Figure 5.3 shows the $T_g$s of the resins containing DGBF and their DGEBA counterparts. As expected the DGBF resins have lower $T_g$s; however, as the $T_g$ decreases, the effect of DGBF decreases. For these lower $T_g$ resins, there is already a significant portion of the network that is flexible (over 40% in D400) so a slight increase in flexibility has a minor impact. On the other hand, for DGEBA with PACM, there is very little flexibility in the system. Introducing the slight flexibility of DGBF decreases the $T_g$ by over 30 °C.

This flexibility does not manifest itself much in the 30°C modulus, shown in Table 5.4. Only B440 shows more than 100 MPa difference between the epoxies, but even this difference is fairly minor. The molecular weights between cross-links show
interesting behavior. With slightly higher functionality (2.17 epoxies per molecule), one would expect the $M_c$ for the DGEBF to be slightly lower, meaning higher cross-link density. Instead, for all resins, $M_c$ is approximately 90 g/mol higher. In Chapter 3 the higher than expected $M_c$ values were well explained by assuming an imperfect network. A similar situation could be the cause of these results. If the central epoxy group, present on almost every fifth epoxy molecule, reacted with the same amine as one of the ends, but the 2-functional epoxies reacted with two distinct amines, the expected $M_c$ would be higher than for the DGEBF resins than for DGEBA, calculating $M_c$ similar to eq. 3.29. If loop defects were also included, as in eq. 3.30 the DGEBF resins would still have a higher expected $M_c$. 
Figure 5.3: $T_g$s of resins containing DGEBA or DGEBF cured with the same amines.

Table 5.4: Modulus and $M_c$ of resins containing DGEBA and DGEBF cured with the same amines.

<table>
<thead>
<tr>
<th>Resin</th>
<th>$30^\circ C$ Modulus (MPa)</th>
<th>$M_c$ (g/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>DGEBA</td>
<td>DGEBF</td>
</tr>
<tr>
<td>PACM</td>
<td>2360 ± 100</td>
<td>2540 ± 140</td>
</tr>
<tr>
<td>D230</td>
<td>2630 ± 20</td>
<td>2530 ± 140</td>
</tr>
<tr>
<td>B270</td>
<td>2610 ± 100</td>
<td>2530 ± 90</td>
</tr>
<tr>
<td>D400</td>
<td>2640 ± 40</td>
<td>2580 ± 30</td>
</tr>
<tr>
<td>B440</td>
<td>1890 ± 50</td>
<td>1660 ± 30</td>
</tr>
</tbody>
</table>

5.3.2 Linear Epoxies: GPC

The GPC data was analyzed in the same manner as the polydisperse epoxies, described in Chapter 4. The results for the linear epoxies are shown in Figure 5.4 and
Table 5.5. PPGGE380 had two overlapping main peaks around 15 minutes corresponding to 572 and 396 g/mol with a smaller peak at 15.4 minutes corresponding to 258 g/mol. These translated into a $M_n$ of 377 g/mol, which is very similar to the number obtained by doubling the EEW obtained by titration. The polydispersity of 11.8 is high, but the match between $M_n$ and twice the EEW indicated that there are, on average, two epoxy groups per molecule. PPGGE640, on the other hand, had a somewhat broad peak around 14 minutes and two smaller peaks between 16 and 18 minutes. These correspond to molecular weights of approximately 983, 101 and 63 g/mol, respectively, yielding a $M_n$ of 316 g/mol. Those low molecular weights most likely represent unreacted or partially reacted species such as propylene oxide (58 g/mol), propylene glycol (76 g/mol), propylene glycol glycidyl ether (132 g/mol), or 2-(2-hydroxypropoxy)-1-propanol (134 g/mol). Ignoring these low molecular weight species changes the $M_n$ to 912 g/mol. Neither $M_n$ calculation from GPC is similar to twice the EEW, which was supplied by the manufacturer and verified by titration. This suggests that PPGGE640 is not really a diglycidyl ether but a mixture of mono- and diglycidyl ethers.

The PEGGE2000 was not tested by GPC as it was the only epoxy to have polydispersity information provided by its manufacturer. The titrated values for EEW matched the manufacturer’s data.
Table 5.5: Molecular weights of PPG and PEG based epoxies.

<table>
<thead>
<tr>
<th>Resin</th>
<th>$M_n$ (g/mol) (2x EEW)</th>
<th>$M_n$ (g/mol) (GPC)</th>
<th>PDI (GPC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPGGE380</td>
<td>371</td>
<td>377</td>
<td>11.8</td>
</tr>
<tr>
<td>PPGGE640</td>
<td>640</td>
<td>316 or 912†</td>
<td>45.3 or 15.7†</td>
</tr>
<tr>
<td>PEGGE2000</td>
<td>2142</td>
<td>2148*</td>
<td>1.1*</td>
</tr>
</tbody>
</table>

†calculated by ignoring species ≤100 g/mol

*from manufacturer’s certificate of analysis

5.3.3 Linear Epoxies: Extent of Cure

Figure 5.5 shows the FTIR spectra of all the resins in Table 5.2, except for PEGGE2000-PACM and those cured with D230, along with the uncured mixtures of
PPGGE380-PACM. In all of the resins the epoxy and amine peaks are no longer visible after post curing, signifying near complete reaction. The PEG2000-PACM sample is not included in Figure 5.5 as it is not IR transparent. The lack of transparency is due to its crystallinity. DSC was used to investigate the crystallinity and Figure 5.6 shows the DSC scans of all resins containing PEGGE2000. The epoxy by itself shows a melting point near 50 °C and readily recrystallizes. The PEGGE2000-PACM’s crystals melt, although the network remains cross-linked, at a slightly lower temperature and also recrystallizes after cooling. The PPGGE380-PEGGE2000-PACM initially shows a melting point similar, but weaker compared to the neat epoxy or the PEGGE2000-PACM. After cooling, the network has a broad melting peak at lower temperature. This is visibly evident in the increased transparency at elevated temperatures as shown in Figure 5.7. Table 5.6 summarizes the amounts of crystallinity present in the systems, as calculated from DSC.
Figure 5.5: FTIR spectra of PPG-epoxies, freshly mixed and after post cure. Spectra have been shifted vertically for clarity.
Figure 5.6: DSC scans of PEGGE2000 containing resins. The PPGGE380-PEGGE2000-PACM scan was enhanced 10x.

Table 5.6: Percent crystallinity of PEGGE epoxies.

<table>
<thead>
<tr>
<th></th>
<th>T_{\text{melting}} (°C)</th>
<th>Crystallinity (%)</th>
<th>Crystallinity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Overall</td>
<td>of PEGGE</td>
</tr>
<tr>
<td>PEGGE2000</td>
<td>54 (initial)</td>
<td>100 (assumed)</td>
<td>100 (assumed)</td>
</tr>
<tr>
<td>PEGGE2000-PACM</td>
<td>50 ± 1</td>
<td>54 ± 5</td>
<td>57 ± 5</td>
</tr>
<tr>
<td>PPGGE380-PEGGE2000-PACM</td>
<td>52</td>
<td>&lt; 1</td>
<td>&lt; 1</td>
</tr>
</tbody>
</table>
Figure 5.7: Sanded sample of PEGGE2000-PACM A) room temperature and B) 80 °C. The sanding reduced overall transparency.

### 5.3.4 Linear Epoxies: DMA Properties

Table 5.7 shows the DMA properties of the resins with linear epoxies. PPGGE640 was cured with the widest variety of amines in attempts to find the highest $T_g$, for ease of sample preparation and testing. Whether cured with PACM, MPACM, or PDA, the resulting $T_g$ was approximately -20 °C. This suggests that the size difference between PDA and PACM or MPACM is insufficient to cause any appreciable stiffening effect on the network when paired with a large flexible epoxy. As the FTIR results showed complete reaction for all of those formulations, PACM was chosen as the curing agent for the other linear epoxies, due to its lower temperature cure requirements.

As the length of the epoxy increases, the $T_g$ decreases, as could be expected, with a 40 °C different between PPGGE380-PACM and PPGGE640-PACM; increasing the
epoxy to the PEGGE2000 only results in a $T_g$ drop of another 20 °C. The larger difference between PPGGE380 and 640 rather than PPGGE640 and PEGGE2000 could be due to either the molecular weight distribution of the PPGGE640 or to the crystallinity of the PEGGE2000 skewing the $T_g$ of the PEGGE2000-PACM. Figure 5.8 shows the storage and loss moduli of the PPG and PEG based epoxies cured with PACM. In the two resins containing the PEG epoxy, it is clear how the crystallinity affects the modulus and $T_g$. The PEGGE2000-PACM sample retains a much higher modulus than the others up to the melting point of PEG, ~50 °C. Previous research involving crystalline thermosets tended to be restricted to liquid crystal epoxies where the epoxy itself is the mesogenic unit [6-8] although some work included an aromatic diamine which contained the mesogenic unit [9]. Those resins required much higher processing temperatures, up to 190 °C [9]. The fracture toughness of liquid crystalline epoxies has been reported to be double that of the isotropic version [10] and the crystallinity is expected to increase the fracture toughness here as well; however, due to the low $T_g$ and high cost of the PEGGE2000, those tests were not performed.

For PPGGE380 and PPGGE640 both cured with D230, it is interesting their $T_g$s are different by over 20 °C. Work in chapter 3 showed that the $T_g$ tracked linearly with the PPG-based amine content. If that trend applies to these samples, then both of these samples containing only PPG-based components would be expected to have similar $T_g$s. However, the trend from Chapter 3 was based on lower cross-link density with increasing PPG content. Here there are simply two resins with similar PPG-based content but different cross-link densities. In addition the molecular weight distribution of the PPGGE640 could further separate the $T_g$s. As mentioned in section 5.3.2, it appears that
mono-functional species are present in the PPGGE640, these would reduce the cross-link density and hence the $T_g$.

Figure 5.8: Loss (top) and storage modulus (bottom) of linear epoxies cured with PACM shifted to $T_g$. 
5.3.5 Blends of Linear and Aromatic Epoxies: DMA

All of the linear epoxies, regardless of curing agent, had $T_g$s at or below room temperature; therefore, none of these samples were tested for fracture toughness. The addition of Epon 825 to PPGGE380 and PPGGE640 was done to A) change the rigid/flexible ratio in a controllable manner and B) increase the $T_g$ to create samples more suitable for fracture testing. The results are shown in Table 5.8 and Figure 5.9. Below a PPGGE volume fraction of approximately 0.75, the $T_g$s increased almost linearly with respect to the decreasing PPGGE volume fraction, neglecting chain ends, as does the peak in tan $\delta$. In contrast to the $T_g$, the glassy modulus (at $T_g$ -50 °C) increases linearly with PPGGE content until 0.6 volume fraction for PPGGE380 and 0.75 for PPGGE640. Trend lines of the linear regions of the $T_g$s resulted in $R^2$ values greater than 0.98. These were used to predict formulations with $T_g$s similar to 825-D400 (54 °C). 825-D400 was chosen as a comparison as other comparisons to it, i.e. B390 and B440, have already been
analyzed. The PPGGE380/825 blend matched 825-D400’s $T_g$ quite well, within 3 degrees of the target $T_g$, while the PPGGE640/825 blend was approximately 10 °C lower, resulting from slightly more scatter in the data used for the prediction.

Table 5.8: DMA properties of linear epoxies blended with DGEBA and cured with PACM.

<table>
<thead>
<tr>
<th>Molar Ratio of Epoxy</th>
<th>Storage Modulus $T_g$ $-50^\circ$C (MPa)</th>
<th>$T_g$ (°C)</th>
<th>Tan $\delta_{max}$ (°C)</th>
<th>PPGGE Volume Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPGGE380/825</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>100/0</td>
<td>3040 ± 60†</td>
<td>20.3 ± 0.9</td>
<td>29.5 ± 0.9</td>
<td>0.748</td>
</tr>
<tr>
<td>75/25</td>
<td>3390 ± 40</td>
<td>44.5 ± 1.4</td>
<td>53.6 ± 1.0</td>
<td>0.570</td>
</tr>
<tr>
<td>65.3/34.7*</td>
<td>3450 ± 80</td>
<td>51.3 ± 1.5</td>
<td>63.3 ± 0.5</td>
<td>0.499</td>
</tr>
<tr>
<td>50/50</td>
<td>2690 ± 50</td>
<td>72.5 ± 1.8</td>
<td>84.6 ± 1.1</td>
<td>0.386</td>
</tr>
<tr>
<td>25/75</td>
<td>1940 ± 50</td>
<td>115.4 ± 0.9</td>
<td>125.5 ± 0.4</td>
<td>0.196</td>
</tr>
<tr>
<td>0/100</td>
<td>1470 ± 80</td>
<td>168.3 ± 1.2</td>
<td>176.7 ± 0.9</td>
<td>0</td>
</tr>
<tr>
<td>PPGGE640/825</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>100/0</td>
<td>3140 ± 10†</td>
<td>-19.6 ± 0.8</td>
<td>-10.2 ± 0.8</td>
<td>0.849</td>
</tr>
<tr>
<td>90/10</td>
<td>3620 ± 160</td>
<td>-18.8 ± 0.7</td>
<td>-8.5 ± 1.1</td>
<td>0.798</td>
</tr>
<tr>
<td>80/20</td>
<td>3940 ± 70</td>
<td>-13.2 ± 0.8</td>
<td>-0.4 ± 1.0</td>
<td>0.744</td>
</tr>
<tr>
<td>75/25</td>
<td>3860 ± 70</td>
<td>-6.7 ± 1.9</td>
<td>7.6 ± 2.4</td>
<td>0.714</td>
</tr>
<tr>
<td>50/50</td>
<td>3530 ± 40</td>
<td>17.5 ± 1.8</td>
<td>40.4 ± 0.7</td>
<td>0.542</td>
</tr>
<tr>
<td>37.6/62.4*</td>
<td>3330</td>
<td>44.3 ± 0.4</td>
<td>62.0 ± 0.3</td>
<td>0.438</td>
</tr>
<tr>
<td>25/75</td>
<td>2420 ± 40</td>
<td>73.5 ± 1.4</td>
<td>91.2 ± 0.2</td>
<td>0.315</td>
</tr>
<tr>
<td>0/100</td>
<td>1470 ± 80</td>
<td>168.3 ± 1.2</td>
<td>176.7 ± 0.9</td>
<td>0</td>
</tr>
</tbody>
</table>

*Blends calculated to match the $T_g$ of 825-D400
†From samples with S-T<10
5.3.6 Fracture Toughness

Fracture samples of the 825-D400-matching blends containing PPGGE are summarized in Table 5.9 along with those of 825-D400 from Chapter 3 for comparison. The PPGGE380/825/PACM blend matches 825-D400 almost exactly. The PPGGE640/825/PACM blend has higher toughness values and the fracture behavior shifts from brittle stable to unstable; however, its $T_g$ is also lower. Also listed in Table 5.9 are the fracture properties of the resins containing DGEBF as well as that of 825-PACM. As with the previous resins containing Epon 825, there is an increase in toughness with decreasing $T_g$ and the fracture behavior transitions from brittle-stable to
unstable. All of the resins from Table 5.9 are shown in the top part of Figure 5.10. The bottom portion of Figure 5.10 includes the data from the other Jeffamine formulations from Chapter 3 and a representative polydisperse epoxy from Chapter 4. The toughness of the PPGGE/825/PACM blends fits the pattern of the previous results, including the higher fracture toughness of the PPGGE640/825/PACM blend. This shows that moving the flexible portion from the amine, D400 or a D230/D2000 mixture, to the epoxy, PPGGE, makes no difference in the overall network. The only samples that do not fit the general trend of the others are 825-PACM and BisF-PACM. They show unstable-stick-slip behavior despite being tested very far from their \( T_g \); however, these are also the only samples with the least flexibility in the network.

Table 5.9: Fracture properties of 825-PACM, PPGGE/825/PACM blends with \( T_g \)s similar to 825-D400 and samples with DGEBF cured with Jeffamines and PACM.

<table>
<thead>
<tr>
<th>Resin</th>
<th>Testing ( T ) (°C)</th>
<th>( T - T_g ) (°C)</th>
<th>( K_{1c} ) (MPa m^{1/2})</th>
<th>( G_{1c} ) (J/m^2) (from area)</th>
<th>( G_{1c} ) (J/m^2) (from ( K_{1c} ))</th>
<th>Facture Behavior</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPGGE380/825/PACM</td>
<td>0</td>
<td>-52.3</td>
<td>0.79 ± 0.07</td>
<td>170 ± 30</td>
<td>160 ± 30</td>
<td>S</td>
</tr>
<tr>
<td>PPGGE640/825/PACM</td>
<td>0</td>
<td>-44.3</td>
<td>1.18 ± 0.10</td>
<td>390 ± 70</td>
<td>390 ± 70</td>
<td>U</td>
</tr>
<tr>
<td>D400</td>
<td>0</td>
<td>-54</td>
<td>0.82 ± 0.08</td>
<td>250 ± 40</td>
<td>210 ± 40</td>
<td>S</td>
</tr>
<tr>
<td>BisF-PACM</td>
<td>23</td>
<td>-106.4</td>
<td>0.82 ± 0.04</td>
<td>230 ± 10</td>
<td>230 ± 20</td>
<td>U-SS</td>
</tr>
<tr>
<td>BisF-D230</td>
<td>23</td>
<td>-62.6</td>
<td>0.82 ± 0.08</td>
<td>230 ± 10</td>
<td>260 ± 50</td>
<td>S-U-SS</td>
</tr>
<tr>
<td>BisF-D400</td>
<td>23</td>
<td>-29.1</td>
<td>1.01 ± 0.09</td>
<td>340 ± 70</td>
<td>410 ± 80</td>
<td>U-SS</td>
</tr>
<tr>
<td>BisF-B440</td>
<td>23</td>
<td>-32.4</td>
<td>1.31 ± 0.10</td>
<td>1060 ± 180</td>
<td>890 ± 130</td>
<td>U</td>
</tr>
<tr>
<td>825-PACM</td>
<td>23</td>
<td>-147.1</td>
<td>0.83 ± 0.08</td>
<td>230 ± 100</td>
<td>270 ± 50</td>
<td>U-SS</td>
</tr>
</tbody>
</table>

S = Brittle-Stable U-SS = Unstable Stick-Slip U = Unstable
Figure 5.10: Top) fracture toughness of PPGGE/825/PACM blends, DGEBF-Jeffamines and DGEBA-PACM. Bottom) As above plus the 825-Jeffamines from Chapter 3 and a representative polydisperse epoxy from Chapter 4. Fracture type is indicated by color: Orange: brittle-stable fracture; Blue: stable-unstable; Green: unstable stick-slip; Red: unstable.
5.3.7 Combined Results

The fracture results from this and previous chapters, in general, follow the same trends. In Chapter 3 linear trends were seen in T_g versus the amine volume fraction. In this chapter T_g is linear up to a PPGGE volume fraction of approximately 0.75, after which it is there is little change. If instead the volume fraction of the flexible portion, here considered to be an epoxy or amine based on PPG or PEG, is considered, then a single plot can be constructed. Instead of T_g, as was used previous, the peak in the tan δ curve versus flexible volume fraction is shown in Figure 5.11. The peak of tan δ is used as it yields less scatter, mainly from 0.6-0.8 volume fractions than T_g does, due to some very broad transitions in that region, e.g. 825-B1000-D230. As mentioned previously for the PPGGE-825-PACM blends, and valid of other resins as well, the linear trend breaks down above a flexible volume fraction ~0.75. Interestingly it appears to flatten, although PPGGE380 and PPGGE640 each cured with D230 have tan δ peaks, and T_g's, different by over 20 °C. On the low flexible volume side, the trend also breaks down, with 825 and DGEBF each cured with PACM having T_g and tan δ_max different by almost 30 °C. As mentioned previously, DGEBF is more flexible due to no central methyl groups but the slightly higher functionality can restrict some of that, thus flexibility to the DGEBF-PACM system is not assigned.
Figure 5.11: Temperature of the maximum in $\tan \delta$ versus flexible volume fraction for all resins.

$T_g$ has often been related to the cross-link density of polymer. Fox and Loshake [11] related $T_g$ to the molecular weight of lightly cross-linked polymers through equation 5.1:

$$T_g \approx T_{go} - \frac{K}{M} + K_x \nu$$  \hspace{1cm} 5.1

where $T_{go}$ is the $T_g$ of the uncross-linked polymer with infinite molecular weight, $M$ the chain molecular weight, $K$ and $K_x$ are related to the polymer’s specific volume. A more complicated version where the cross-links are a different molecule, as in these networks
was also derived. Later Nielsen compiled numerous results and arrived at the semi-empirical equation 5.2 [12]:

\[ T_g = T_{g^\infty} - \frac{3.9 \times 10^4}{M_c} \]  \hspace{1cm} 5.2

For a DGEBA-based system cured with DDM (4,4'-diaminodiphenomethane) Banks and Ellis [13] derived equation 5.3:

\[ T_g = T_{g^\infty} + \frac{\zeta}{M_n} \]  \hspace{1cm} 5.3

where \( \zeta \) is dependent upon the ratio of the rate of change in free volume of the amine compared to that of the epoxy, the molecular weight of the epoxy repeat unit, and the \( T_g \) of a hypothetical polymer of infinite molecular weight with a monomer based on the amine. Others came to equations of similar form for cross-linked polystyrene [14-15].

More recently Lesser and Crawford used equation 5.3 except replaced \( M_n \) with \( M_c \) [16-17]. For resins with tetra-functional and tri-functional aliphatic amines, plots of \( T_g \) vs. \( \frac{1}{M_c} \) resulted in separate linear trends, as did a mixture of those two types of amines. By scaling \( \frac{1}{M_c} \) by a functionality-based term, the tetra, tri, and mixed-functional amine resins collapsed on a single line [16]; however if aromatic and aliphatic amines were compared, they could not be collapsed on a single curve [17].

Here the peak of the \( \tan \delta \) curve is plotted versus \( 1/M_c \) in Figure 5.12, \( \tan \delta_{\text{peak}} \) is sometimes used as a measure of \( T_g \). Data from diamine propane (DAP) and 1,3-phenylene diamine (PDA) from the DMA study in Chapter 2 are included for additional data at low \( M_c \). Most of the data collapse onto a single curve that starts out very linear.
The points with the lowest \( M_c \) values, 825-PACM, 825-DAP, and 825-PDA, are the ones that deviates from the linear trend the most. The 25/75 PPG380/825-PACM blend also appears to deviate. Fox and Loshaek stated that the linear increase of \( T_g \) with increasing cross-link density will fail at high cross-link densities, with the rate of increase decreasing [11]. Linear regression of all points with \( 1/M_c < 2 \) yields \( T_{g_\infty} = -44 \, ^\circ C \) (228 K) and \( \zeta = 89 \, K \, kg/mol \). Additional linear regressions for all data and the data in Chapters 3, 4, and 5 (everything excluding PDA & DAP) are also shown in Figure 5.12. Crawford and Lesser reported \( \zeta \) being higher for aliphatic than aromatic amines with the same epoxy but both of those were much lower than the number reported here; their aliphatic amines were much shorter [16-17]. For the work here a \( T_g \) for an uncross-linked network of -44 \( ^\circ C \) also agrees quite well with Figure 5.11, as the flexible fraction increases, the cross-link density decreases and the \( T_g \) plateaued in the -20 - -40 \( ^\circ C \) range.
5.4 Conclusions

Several alternative epoxy-amine structures were investigated. These included bisphenol F, poly(propylene glycol), and poly(ethylene glycol) based epoxies. Amine variations included PACM, and MPACM, cyclic amine, and 1,3 phenylene diamine. Unlike previous chapters, here a flexible portion was added to the epoxy portion of the resin. In general the added flexibility manifests in reduced $T_g$ and higher $M_c$, without regard of its position in the network. The results with these alternative epoxies and amines along with results from the previous two chapters can be superimposed to one curve in two ways. $\tan \delta_{\text{peak}}$ versus flexible volume fraction yields a single curve that is
linear up to ~0.8 volume fraction, with the tan $\delta_{\text{peak}}$ approaching -44 °C for an uncross-linked system. Tan $\delta_{\text{peak}}$ versus $1/M_c$ results in a linear trend except at high values (low $M_c$).

For fracture properties, resins with some flexibility — here controlled by PPG backbones, the fracture toughness and fracture behavior is most heavily dependent on the $T_g$ and the difference between $T_g$ and testing temperature, not the specific network structure. Resins made with PEG-based epoxies retain some residual crystallinity after reaction. This residual crystallinity provides rigidity at temperatures well above the peak in the loss modulus.


Chapter 6: Glass Reinforcement

6.1 Introduction

The previous chapters showed that the toughness of epoxies containing poly(propylene glycol)-based monomers is most heavily influenced by the $T_g$ and the difference between $T_g$ and the testing temperature. Blends do introduce heterogeneity to the system and can change the fracture type from brittle-stable to unstable. This chapter explores using that heterogeneity in conjunction with a more traditional secondary phase toughening method.

Epoxy-amine networks are frequently used with a secondary phase to provide enhanced toughness. These include silica [1-2], reactive phase-separating rubber [3-5], pre-formed rubber particles [6], and glass beads [7-8]. Lee and Yee investigated the influence of matrix toughness when toughened with glass beads [7]. They added 10 vol% glass spheres, diameter approximately 25 μm, to a series of resins with increasing molecular weight of the epoxy portion. The $M_c$ calculated from rubbery modulus data ranged from 440 to 5400 g/mol. The same amine was used in all resins. In all cases the added glass increased the fracture toughness and as the $M_c$ increased, the ratio of toughened/untoughened $K_{1c}$ also increased. This was attributed to the change in matrix toughness.

An analogous study was performed using some of the amine bimodal blends from Chapter 3. The amine blends create heterogeneity in the network, despite an average $M_c$
similar to single amine blends. By tailoring the distribution of the amines, the matrix
toughness in the vicinity of the glass beads can be altered. If Lee and Yee’s results are
applicable to the system used here, then a higher molecular weight amine surrounding the
glass beads should yield a greater increased toughness than if lower molecular weight
amine surrounds the beads. Two resin formulations with similar average AHEWs,
described in Chapter 3, were chosen for this study: D400 and B440. For D400 there is
only a single amine while for B440 either D230 or D2000 could preferentially be placed
at the glass-matrix interface. The tailoring of the interface was accomplished using
epoxy functionalized glass beads at a loading of 10 vol%. Plain glass beads were also
used as a control at the same loading. The naming scheme will be D400 or B440
followed by the amine first in contact with the beads if more than one amine was used,
and either epGlass or plGlass for epoxidized and plain glass beads, respectively. In
addition, samples were made using D2000 at the interface, embedded in a D400 matrix.

6.2 Experimental

6.2.1 Materials

As in previous chapters, Epon 825, a high purity DGEBA, was obtained from
Momentive and the Jeffamines were obtained from Huntsman. Spheriglass® A-glass
beads (soda-lime), both plain and epoxy functionalized, were provided by Potters
Industries LLC.
6.2.2 Glass Sphere Characterization

The as received beads contained free iron particles. Before any analysis or use, free iron was removed with a magnet. In certain cases, washed beads were used. The beads were stirred in deionized water overnight then allowed to settle. The supernatant was decanted and the remaining beads were dried at 125 °C.

6.2.2.1 Particle Size Analysis

The diameters of the glass beads are reported to be 30-50 µm. To better quantify the size and distribution, the beads were imaged at 20 x magnification using a Keyence VK-X200 3D Laser Scanning Microscope and the resulting images were analyzed using ImageJ’s particle size analysis function; over 1400 particles of each bead type were measured.

6.2.2.2 Titration

The epoxy-functionalized glass beads are functionalized with an epoxy silane. The exact process and resulting surface functionality are proprietary and were not disclosed by the manufacturer. In attempt to quantify the number of epoxy groups on the glass beads, epoxy titration described in ASTM D1652 [10] was performed on the plain and functionalized beads.

6.2.2.3 FTIR

Due to the low concentration of epoxy groups, mid-IR was used instead of NIR as was used in previous chapters. A SmartOrbit diamond attenuated total reflectance (ATR) accessory was used with a Nicolet Nexus 870 FTIR to take spectra of the beads, with 64 scans at 4 cm⁻¹ resolution per spectrum, with no sample preparation necessary.
6.2.2.4 X-ray Photoelectron Spectroscopy (XPS)

Near-surface compositional measurements were conducted by X-ray photoelectron spectroscopy (XPS), using a Kratos Axis Ultra system equipped with a hemispherical analyzer. The sample was irradiated with a 150 W monochromatic Al Kα (1486.7 eV) beam, and both magnetic and electrostatic lenses were used to select photoelectrons from a 1 mm × 2 mm area of a bed of glass beads with a take-off angle of 90°. The pressure in the XPS chamber was held between 10⁻⁸ and 10⁻⁹ Torr. Elemental high resolution scans for C₁s were acquired in the constant analyzer energy mode with a pass energy of 20.0 eV. A low energy electron neutralizer was employed to reduce surface charging, and the spectra were adjusted for any residual charging by adjusting the energy of the C₁s peak corresponding to C-C to a binding energy of 285.0 eV. Surface compositions were calculated using relative sensitivity factors supplied by Kratos for the Axis Ultra system and the Kratos Vision 2 software. The software was also used to deconvolute the C₁s peak to determine the relative fraction of carbon bonding states present in the sample. Three sets of beads were analyzed: plain beads, washed plain beads, and epoxidized beads.

6.2.3 Sample Preparation

A ratio of 1.002:1 amine hydrogen per epoxy group was used based upon only the resin portion of the samples. A stoichiometric ratio of 1:1 amine hydrogen per epoxy was used for the plain beads. The beads, epoxidized or plain, were allowed to react/interact with the entire amount of one amine at 60 °C overnight. Using the full amount of amine,
a great excess compared to any functionality of the beads, minimizes the chance of an amine fully reacting with the beads.

For the beads functionalized with D2000, the epoxidized beads were allowed to react with an excess D2000 overnight at 60 °C. The beads were allowed to settle and the excess D2000 was decanted off. The beads were then washed with toluene and then ethanol several times to remove unattached D2000 [11]; the beads were allowed to settle and the supernatant was decanted off. After washing, the beads were dried under vacuum at 50 °C.

The other amine, if applicable, was then added and mixed, followed by the epoxy. The resin was mixed by hand and then placed in an 80 °C oven. The resin was mixed again after 30 and 45 minutes, at which point the resin was degassed in a 75-80 °C vacuum oven. The resin was returned to the 80 °C oven and gently stirred periodically to keep the glass beads suspended. Once gelation started to occur, generally 50-60 minutes after adding the epoxy, the resin was poured into an open aluminum mold previously coated with release agent Frekote 55-NC (Henkel), measuring 76 × 102 × 25 mm³ and cured 2 h at 80 °C, removed from the mold, and then posted cured 2 h at 125 °C.

6.2.4 Sample Characterization

6.2.4.1 Thermogravimetric Analysis

Samples were tested via thermogravimetric analysis (TGA) in order to determine the actual glass volume fraction. Small pieces, 10-20 mg, from the bottom of a fracture sample were heated, in air, from room temperature to 1000 °C at 10 °C/min. Only the bottoms of the samples were tested, as the fracture area is the bottom of the as-cast
sample. Measured volume fractions near the target 10 vol% were presumed to have fairly uniform bead dispersion. The actual glass vol% can be calculated by equation 6.1:

\[
Vol\%_{\text{glass}} = \frac{\text{resid}}{\frac{\rho_{\text{glass}}}{\text{resid}} + \frac{\rho_{\text{polymer}}}{1 - \text{resid}}} \times 100\%
\]

where resid is the minimum residual mass percent, \(\rho_{\text{glass}}\) and \(\rho_{\text{polymer}}\) are the densities of glass and the polymer matrix, 2.5 g/cm\(^3\) [9] and 1.14 g/cm\(^3\) from Chapter 3, respectively. TGA tests of the beads alone resulted in < 0.1 % weight loss and this small loss was neglected when calculating glass vol% of the samples.

6.2.4.2 DMA

All samples were also characterized by DMA for the \(T_g\) determination and to measure the modulus at 0 °C for the calculation of \(G_{1c}\). Two single cantilever samples from each fracture block were cut, with nominal dimensions of 35 × 12 × 3 and 35 × 12 × 1.6 mm\(^3\). Samples were tested from 0 °C to 150 °C, with a heating rate of 2 °C/min and 0.02 % strain oscillating at 1 Hz. Data measured from the thin sample provided glassy modulus information while the thicker sample yielded rubbery modulus information; both yielded \(T_g\) data.

6.2.4.3 Fracture Toughness

SENB samples were cut from the 76 × 102 × 18 mm\(^3\) sample block with nominal sample sizes of 8 × 17 × 76 mm\(^3\). A notch was cut, approximately 3 mm deep in the 17 mm direction using a 1 mm thick diamond blade. To generate the starting crack, cut samples and razor blades were first placed in a -20 °C freezer overnight. A sample and a
razor blade were removed from the freezer; the razor blade was placed in the sawn-in notch and tapped with a hammer until a crack propagated, leaving a ligament approximately 8 mm for the crack to propagate through during the test. These were of the “instantly propagated” cracks, as shown by Ma et al. [12] to minimize fracture toughness. Samples were tested at 0 °C on a screw-driven Instron testing frame with a 5 kN load cell according to ASTM D5045 [13] after being conditioned at those temperatures for at least 2 hours. Six to seven samples were tested per formulation. The fracture surfaces were imaged using the Keyence VK-X200 3D Laser Scanning Microscope with no further modification.

6.3 Results and Discussion

6.3.1 Bead Characterization

The diameters of the beads were $30 \pm 12 \, \mu m$ and $22 \pm 9 \, \mu m$ for the plain and epoxidized beads, respectively. The plain beads have a slightly wider overall distribution, as shown in Figure 6.1, but the beads are similar to those used by Lee & Yee [7].
The epoxy titration of the epoxidized beads yielded an epoxy equivalent weight (EEW) of approximately 24,000 g/mol; however, the plain beads yielded an EEW of 16,000 g/mol, a higher apparent concentration of epoxy groups. The glass beads are soda-lime glass and have a basic leachate pH; it is presumed that the basic leachate interfered with the acidic epoxy titration, resulting in invalid data.

6.3.1.1 FTIR

In the MIR, a peak corresponding to the epoxy group appears around 915 cm\(^{-1}\) [14]. Unfortunately, soda-lime glass has a broad peak centered around 1050 cm\(^{-1}\) that can extend from 1200-900 cm\(^{-1}\) that is attributed to Si-O stretching [15]. Figure 6.2 shows the MIR spectra of the plain beads and epoxidized beads, as well as a spectrum of the epoxidized beads that used the plain beads as the background spectrum. The plain beads show a broad peak around 1030 cm\(^{-1}\). The epoxidized beads have strong peak around
910 cm\(^{-1}\), with the 1030 cm\(^{-1}\) peak appearing as a shoulder. Also shown in Figure 6.2 is the spectrum of neat Epon 825. The characteristic epoxy peak at 915 cm\(^{-1}\) is identified and it matches well with the main peak in the epoxidized beads. The spectrum of epoxidized beads using the plain beads as a background shows a peak closer to 900 cm\(^{-1}\); however, the 1030 cm\(^{-1}\) peak can shift due to actual content and thermal history of the glass [15], so it is possible that the shift from ~910 to 895 cm\(^{-1}\) is partially an artifact of subtracting mismatched 1030 cm\(^{-1}\) peaks due to different batches or thermal treatment of the plain and epoxidized beads.
Figure 6.2: FTIR spectra of plain beads, epoxidized beads, epoxidized beads using the plain beads as background spectrum, and Epon 825.

6.3.1.2 XPS

The XPS results are shown in Table 6.1. The appearance of sulfur and fluorine was unexpected and is presumably the result of a surfactant or sizing package used during production. The epoxidized beads have approximately 3% more carbon than the other samples. One might be tempted to dismiss this as being in the noise of the measurement but it can be confirmed by looking at the shape of the carbon 1s peak, shown in Figure 6.3. In XPS, carbon in different chemical bonding environments has slightly different binding energies (C-C, C-O, C=O, C-F, etc) and the entire C$_{1s}$ peak can be deconvoluted
to get the fraction of carbon in each of these states. In this case, the extra 3% of carbon that is found in the epoxy samples occurs entirely in higher energy peaks. Carbon bonded to various oxygen species shifts the peak +1.5-4.0 eV with the epoxide group expected to shift the peak similar amounts as C-OH [16]. Carbon-fluorine bonds are also expected to shift the C\textsubscript{1s} peak ~ +4 eV [17], which makes precise identification of species difficult. However, the peak corresponding to "adventitious carbon", 285 eV, did not change. In Figure 6.3C, the higher energy peaks are clearly stronger relative to the 285 eV C-C peak than in the as-received and washed plain beads.

<table>
<thead>
<tr>
<th>Table 6.1: XPS elemental analysis.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Elements (atomic %)</td>
</tr>
<tr>
<td>Si</td>
</tr>
<tr>
<td>Plain Beads</td>
</tr>
<tr>
<td>Washed Beads</td>
</tr>
<tr>
<td>Epoxidized Beads</td>
</tr>
</tbody>
</table>
Figure 6.3: XPS spectra of the C\textsubscript{1s} peak for A) plain - as received, B) plain - washed, and C) epoxidized glass beads.

Between the XPS and FTIR results, an epoxy functionalized surface is confirmed on the glass beads, although the exact quantities were not able to be verified. Tsyalkovsky et al. covered 150 nm silica with a 3-4 nm thick layer of fluorescent-tagged poly(glycidyl methacrylate) [18]. The epoxide concentration was estimated to be 18 epoxy groups/nm\textsuperscript{2} although with epoxies lost to loops and cross-linking, the effective concentration was estimated to be not less than 5 epoxies/nm\textsuperscript{2}. If the glass beads had
similar surface epoxy concentrations, then based on the measured diameter and a density of 2.5 \( \text{g/cm}^3 \), the effective EEW would be 300,000 to 1,000,000 g/mol. In the formulations, a slight excess of amine was used with the epoxidized beads to account for the epoxy groups on the beads, yet not enough to depress the \( T_g \).

6.3.2 TGA and DMA Results

The measured glass volume percents from TGA results and 6.1 are listed in Table 6.2. All samples are very close to the target of 10 vol\%. The B440 with plain glass mixed with D230 is the only one that shows sign of settling, and that is minimal.

The \( T_g \)s of the samples, from the peak in the loss modulus, are relatively unchanged by the presence of the glass. All of the \( T_g \)s for glass-containing samples were within 3 °C of the neat resins’ \( T_g \)s. The glass does provide reinforcement, manifesting in slightly increased storage moduli at 0 °C. For each resin, the addition of epoxy functionalized glass increased the moduli more than the unfunctionalized ones: an increase of 800 MPa compared to 600 MPa in D400 and 600-700 MPa compared to 300 MPa for the B440, for the functionalized and unfunctionalized, respectively. The D2000+epGlass in the D400 matrix had a modulus increase more similar to that of D400+plGlass rather than D400+epGlass, possibly due to the small amount of D2000 present. Reinforcement is also seen in the rubbery plateau region, although there is no clear difference between the plain and epoxidized glass.
Table 6.2: Actual glass volume percentages and DMA data for glass-filled D400 and B440 samples.

<table>
<thead>
<tr>
<th>Resin</th>
<th>Glass Vol %</th>
<th>$T_g$ (°C)</th>
<th>Storage Modulus (at 0 °C, MPa)</th>
<th>Rubbery Modulus (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D400</td>
<td>0</td>
<td>53.8 ± 0.3</td>
<td>2900</td>
<td>12.2 ± 0.4</td>
</tr>
<tr>
<td>D400+epGlass</td>
<td>9.2</td>
<td>53.1 ± 2.6</td>
<td>3700</td>
<td>16.9</td>
</tr>
<tr>
<td>D400+plGlass</td>
<td>10.2</td>
<td>52.1 ± 1.9</td>
<td>3500</td>
<td>14.5</td>
</tr>
<tr>
<td>D400: D2000+epGlass</td>
<td>10.0</td>
<td>54.5 ± 0.6</td>
<td>3500</td>
<td>16.6</td>
</tr>
<tr>
<td>B440</td>
<td>0</td>
<td>55.6 ± 0.8</td>
<td>2700</td>
<td>12.2 ± 0.6</td>
</tr>
<tr>
<td>B440: D2000+epGlass</td>
<td>9.6</td>
<td>54.7 ± 1.0</td>
<td>3400</td>
<td>17.2</td>
</tr>
<tr>
<td>B440: D2000+plGlass</td>
<td>9.6</td>
<td>56.8 ± 2.9</td>
<td>3000</td>
<td>17.0</td>
</tr>
<tr>
<td>B440: D230+epGlass</td>
<td>9.6</td>
<td>56.0 ± 2.8</td>
<td>3400</td>
<td>17.5</td>
</tr>
<tr>
<td>B440: D230+plGlass</td>
<td>11.6</td>
<td>58.4 ± 1.3</td>
<td>3000</td>
<td>17.5</td>
</tr>
<tr>
<td>B440: both+epGlass</td>
<td>9.7</td>
<td>54.2 ± 1.4</td>
<td>3300</td>
<td>16.9</td>
</tr>
<tr>
<td>B440: both+plGlass</td>
<td>9.2</td>
<td>58.0 ± 1.7</td>
<td>3000</td>
<td>16.2</td>
</tr>
</tbody>
</table>

The moduli of composites are often modeled using the Halpin-Tsai equations, which assume a perfect interface between filler and matrix [19]. The modulus of a composite is given by equations 6.2 - 6.4:

$$E_c = \frac{1 + \zeta \eta \phi}{1 - \eta \phi} E_m$$  \hspace{1cm} \text{6.2}

$$\eta = \frac{E_f}{E_m} - 1$$  \hspace{1cm} \text{6.3}

$$\frac{E_f}{E_m} + \zeta$$
\[ \zeta = 2 \frac{l}{d} \]

where \( E \) is the modulus, \( l \) is the filler particle length, \( d \) is the filler particle diameter, and the subscripts \( c, m, \) and \( f, \) refer to the composite, unfilled matrix, and filler, respectively. For the spherical particles used here, \( \zeta = 2 \).

Using the modulus values for D400 and B440 shown in Table 6.2 and a glass modulus of 69 GPa, the Halpin-Tsai model predicts glassy moduli of 3700 and 3500 MPa for D400 and B440 filled with 10 vol\% glass beads, respectively. For both resins the Halpin-Tsai model predicts a rubbery modulus of 16 MPa. The model predictions for glassy moduli match the experimental values for samples containing epoxidized beads quite well, but overestimate those containing plain beads. This is a result of the bead-matrix interface. The model assumes a perfect interface and the functionalized glass surface of the epoxidized beads provides a better interface than the plain beads. For the rubbery modulus values, adhesion is less important due to strong frictional forces between the matrix and filler [20].

### 6.3.3 Fracture Toughness

The main property of interest for these samples is the fracture toughness and how the beads affect it. Overall there was little effect on the fracture behavior, with all glass-filled samples fracturing unstably with 0-2 arrests. The fracture toughness, \( K_{1c} \), of the resins is shown in Figure 6.4 and in Table 6.3. The samples using plain glass in B440 show the highest overall toughness, with no dependence upon which amine contacted the beads first, as expected, as there was no surface functionalization. The B440: D2000+epGlass and D400: D2000+epGlass also showed very high fracture toughness.
Those were the two samples that placed D2000 at the functionalized glass-matrix interface. When normalized against the unfilled resins (Figure 6.5) D400: D2000+epGlass has the largest increase, with an almost 90% increase, with B440: D2000+epGlass and all three B440+plGlass samples having 65-80% increases. The same trends are seen when comparing $G_{1c}$ values.

![Fracture properties of glass filled D400 and B440 tested at 0 °C.](image)

Figure 6.4: Fracture properties of glass filled D400 and B440 tested at 0 °C.

As with the modulus differences, the fracture properties can also be related to the interface between the matrix and the beads. Figure 6.6 and Figure 6.7 compare the
fracture surfaces of D400 with epoxidized and plain beads. The surfaces of the epoxidized glass beads are rough, covered with the epoxy, while most of the plain beads’ surfaces are smooth. In the plain glass samples with a weak interface, the crack propagates at the interface around the equator of the particles while with a strong interface, the crack propagates through the matrix, as with epoxidized glass [21-22].

Table 6.3: Fracture properties of neat and glass-filled (10 vol %) epoxies, tested at 0 °C.

<table>
<thead>
<tr>
<th>Resin</th>
<th>$K_{1c}$ (MPa m$^{1/2}$)</th>
<th>$G_{1c}$ (J/m$^2$)</th>
<th>$G_{1c}$ from $K_{1c}$ (J/m$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D400</td>
<td>0.82 ± 0.08</td>
<td>250 ± 50</td>
<td>210 ± 40</td>
</tr>
<tr>
<td>D400+epGlass</td>
<td>1.21 ± 0.09</td>
<td>450 ± 40</td>
<td>350 ± 60</td>
</tr>
<tr>
<td>D400+plGlass</td>
<td>1.46 ± 0.11</td>
<td>550 ± 70</td>
<td>540 ± 80</td>
</tr>
<tr>
<td>D400: D2000+epGlass</td>
<td>1.58 ± 0.07</td>
<td>680 ± 80</td>
<td>640 ± 60</td>
</tr>
<tr>
<td>B440</td>
<td>0.99 ± 0.03</td>
<td>410 ± 70</td>
<td>360 ± 30</td>
</tr>
<tr>
<td>B440: D2000+epGlass</td>
<td>1.63 ± 0.10</td>
<td>920 ± 80</td>
<td>690 ± 80</td>
</tr>
<tr>
<td>B440: D2000+plGlass</td>
<td>1.63 ± 0.10</td>
<td>860 ± 100</td>
<td>780 ± 90</td>
</tr>
<tr>
<td>B440: D230+epGlass</td>
<td>1.36 ± 0.08</td>
<td>560 ± 30</td>
<td>480 ± 50</td>
</tr>
<tr>
<td>B440: D230+plGlass</td>
<td>1.77 ± 0.05</td>
<td>990 ± 90</td>
<td>920 ± 50</td>
</tr>
<tr>
<td>B440: both+epGlass</td>
<td>1.36 ± 0.05</td>
<td>560 ± 40</td>
<td>490 ± 40</td>
</tr>
<tr>
<td>B440: both+plGlass</td>
<td>1.62 ± 0.07</td>
<td>880 ± 40</td>
<td>770 ± 60</td>
</tr>
</tbody>
</table>
Figure 6.5: Fracture toughness at 0 °C, normalized to the resins base, unfilled matrix.

For the epoxidized glass beads, the toughening effect comes from crack pinning and deflection [22-23]. The tails following the glass beads in Figure 6.6A and C have been attributed to crack pinning, with more of these tails are visible in Figure 6.6A than in Figure 6.7A, the plain glass sample. Crack deflection results in increased surface roughness as the crack front is tilted/twisted around the particle as visible in Figure 6.6C, and residual resin is seen on the bead [23-24]. In contrast are Figure 6.7C and Figure 6.8C where the beads are smooth and free of resin. For the normalized results, there is a clear trend of increasing $K_{1c}$ with increasing molecular weight of the amine at the
interface. As the molecular weight of the amine at the surface increased, the roughness and associated plastic deformation increases, leading to the higher $K_{1c}$. By functionalizing the beads with D2000 and adding those to a D400 matrix, the samples gain the toughness from a D2000 interface yet retain the higher modulus of D400. These results match well with Lee and Yee’s increased toughness with increased $M_c$ [7], only here $M_c$ only increases in the vicinity of the beads.

Figure 6.6: Microscope images and height profiles for D400 with epoxidized beads: A & B are at 20x while C & D are at 100x magnification.
Figure 6.7: Microscope images and height profiles for D400 with plain beads: A & B are at 20x while C & D are at 100x magnification.
Figure 6.8: Microscope images and height profiles for D400 with D2000 epoxidized beads: A & B are at 20x while C & D are at 100x magnification.

For the plain beads, the interfaces are all weak, as evidenced by the beads that are free of polymer in Figure 6.7. While there is some evidence of crack pinning and deflection, the additional toughening can be attributed to debonding and plastic void growth [25]. Debonded beads are visible in samples with epoxidized beads as well as plain beads, as shown by the blue depressions in Figure 6.6-Figure 6.8 C and D; however more are expected in samples with weak bead-epoxy interfaces. Due to the size distribution of the beads, it is difficult to ascertain the amount of void growth accompanying the debonding. Micrographs of the other samples showing similar results can be found in Appendix II.
6.4 Conclusions

Glass bead reinforced samples were made using either epoxy-functionalized beads or plain beads. For the functionalized beads, one amine was preferentially reacted with the beads, allowing for a tailored interface. Neither type of bead nor tailoring of the interface altered the $T_g$ of the samples yet the epoxidized beads provided more reinforcement, as measured by higher storage moduli.

Substantial increases in fracture toughness were achieved by simply adding plain glass beads. The greatest increase in toughness came with D2000 modified glass beads in a D400 matrix. This combination leveraged the high modulus from a non-blended amine yet gained the toughness by allowing deformation in the local vicinity of the beads.
List of References


Chapter 7: Summary, Conclusions, and Future Work

7.1 Summary

Epoxies are commonly used in high performance composites because of their high moduli, $T_g$s, and ease of processing. Generally these favorable mechanical properties are offset by poor fracture resistance. To overcome these limitations, epoxies are toughened with a secondary phase. The secondary phase is most often a reactive phase separating rubber but other toughening agents are also used. Innate toughening of the epoxies is desirable to limit the dependence on secondary toughening agents.

The objective of this work was to improve the fracture properties of untoughened epoxies through intelligent changes in the network structure. Several approaches to this goal were proposed: bimodal distributions in the epoxy or amine side, linear epoxies and other structures.

Chapter 2 focused on two experimental techniques: dynamic mechanical analysis and fracture testing. DMA is a very common analytical tool for polymers but the dependence on sample size is not well known. Five epoxy resins with a range of $T_g$s were tested on three different clamps with thickness variations to observe the influence of thickness on modulus and $T_g$ results. Size and clamp type guidelines were proposed in order to obtain the most accurate data. A literature survey showed that many researchers report data that were measured outside the sensitivity limits of the DMA instrument as well as sample sizes ill-suited to measure the properties that were reported.
Chapters 3 and 4 presented experimental data for epoxy-amine networks with distributions on the amine and epoxy side, respectively. Distributions in molecular weight of a DGEBA-type epoxy were shown to have little impact on the overall network. On the other hand, bimodal distributions of flexible amines coupled with DGEBA resulted in broader \( T_g \)s, changes in the fracture behavior, and less temperature dependence. The difference between these two results appeared to be due to the flexibility or lack thereof in the monomer with the controlled distribution.

Chapter 5 presented the effects of other structural variations on the network. Replacing DGEBA with DGEBF resulted in decreased \( T_g \), but no change in fracture properties once the decrease in \( T_g \) was considered. For linear epoxies, the resulting properties were similar to those using linear amines at similar flexible volume fractions. Two samples used PEG-based epoxies. These samples retained some crystallinity after the network had formed. This residual crystallinity provided reinforcement to the polymer well above its \( T_g \). The crystallinity could be melted and reformed.

Also in Chapter 5, the results from Chapters 3, 4, and 5 were combined. Provided there is some flexibility in the network, the fracture toughness follows the same trend. The breadth of the flexibility can alter the fracture behavior, e.g. from brittle-stable to unstable slip-stick. Flexibility that is only present as part of the bisphenol structure (DGEBA vs. DGEBF), exerts no change on the fracture properties, other than a shift with \( T_g \).

In Chapter 6 glass beads were added to the resin as a secondary toughening phase. The surfaces of some of the beads were epoxy functionalized, allowing for the bead-matrix interface to be controlled. When the beads were functionalized, the fracture
toughness increased with increasing molecular weight of the interfacial amine. When the beads were unfunctionalized, there was no dependence on amine molecular weight and the samples had higher fracture toughness.

7.2 Conclusions

The DMA study concluded that the single cantilever clamp is the preferred testing geometry for epoxy networks, and presumably for thermosets in general. A sample span-to-thickness ratio > 10 should be used to ensure accurate glass modulus measurements while for good rubbery modulus data the sample must be thick enough to be within the instrument’s stiffness sensitivity limits.

When testing the fracture toughness of epoxies, “instantly propagated” cracks are the preferred type of starter crack. In many instances they can be is difficult to generate, but they guarantee a sharp crack tip.

In general, T-T_g is the dominating factor determining the fracture toughness of untoughened epoxies. Epoxy samples that contain any amount of a flexible monomer follow the same general trend with increasing fracture toughness as the testing temperature approaches T_g. Distributions in molecular weight in the more rigid portions of the network have little effect while distributions in the linear/flexible portion can alter the fracture behavior from unstable to unstable stick-slip and decrease the dependence on the testing temperature.

Heterogeneity in the molecular weight between cross-links (M_c) caused by molecular weight distributions can be exploited in glass bead toughened resins to increase fracture toughness. When the areas of high M_c are preferentially located at the bead-
matrix interface the fracture toughness is greatly improved. Glass beads bonded to a high molecular weight amine can introduce local heterogeneity in an otherwise monodisperse amine network to achieve increased toughness, without causing a decrease in the bulk $T_g$ or modulus.

### 7.1 Recommendations for Future Work

#### 7.1.1 Yield Stresses

Throughout this dissertation, fracture toughness tests exhibited different types of fracture behavior ranging from brittle-stable to slip-stick to unstable fracture. While the transitions between fracture behavior has been attributed to changes in curing agent, cure schedule, filler content, test rate, and test environment [1], in this work is it most likely controlled by the yield stress, which is dependent upon the testing temperature and rate. A thorough study on the yield stresses of the resins and blends of this work would be beneficial to understanding these fracture transitions. Bulk yield stress can be measured either in tension [2] or compression [3]. For mode I fracture, the tensile yield stress is more applicable; however, it can be difficult to measure in epoxy samples as they often fracture before yielding. In those cases 0.7 times the compressive yield stress is often used as a conservative estimate [4]. In addition to the bulk yield stress, quantifying the variation in the local yield stresses due to network heterogeneity would be informative. For example in a sample that exhibits slip-stick fracture, the yield stress in the “stick” regions may be different than in the “slip” regions. One method to probe the local properties is through the use of atomic force microscopy (AFM). AFM can be used to
determine modulus at the nanometer level [5]. Other AFM techniques can quantify the local changes in $T_g$ as well as the yield stresses [6].

### 7.1.2 Non-Quasi-static Fracture Toughness

Most fracture toughness testing, including that included in this work, is performed quasi-statically. Extending the testing regime to higher strain rates can provide additional data, especially for application that are expected to experience high strain rate impacts. High strain rate behavior can be partially characterized by measuring the $V_{50\text{BL}}(P)$ – a ballistic limit protection criterion. $V_{50\text{BL}}(P)$ is the velocity at which there is a 50% probability of penetration of an aluminum foil witness target behind the sample through transfer of fragments onto the witness target, or complete penetration of the sample and witness target by the incoming projectile [7]. The effective strain rates for impact in $V_{50}$ testing are $10^4$-$10^5$ s$^{-1}$, approximately $10^5$ times greater than in quasi-static testing.

Results for some of the resins investigated in the work, and similar resins have been published [8]. When tested at room temperature, for samples with sub-ambient $T_g$s (or tan $\delta_{\text{peak}}$ as was used in the reference), i.e. rubbery samples, the $V_{50}$ values are quite low, while samples that are glassy at room temperature all had relatively the same $V_{50}$ value, despite differences in $T_g$, monomer structure, functionality, and sub-$T_g$ relaxations. When the $T_g$ of a sample is near room temperature, $V_{50}$ increases and reaches a maximum, as shown in Figure 7.1. Work is currently underway to extend the testing temperature range as well as test other resin systems.
7.1.3 Crystalline Epoxies

The partially crystalline samples from Chapter 5 also suggest a path for future research. Common liquid-crystal epoxies require much higher processing temperatures that what was used in Chapter 5, up to 190 °C [9]. In addition, the fracture toughness of liquid-crystal epoxies has been reported to be double that of the isotropic version [10]. The samples from Chapter 5 retained, at most, 57% of the theoretical crystallinity. Despite this relatively low crystallinity and a $T_g$ of -40 °C, the sample retained a storage
modulus greater than 200 MPa up to 40 °C, 80 °C higher than the $T_g$. As the sample was composed of > 95 vol% PEGGE2000, if the crystallinity were higher, the retained modulus above $T_g$ would also have been higher. An ideal crystalline epoxy system would have a higher $T_m$ but also a higher degree of crystallinity. The 825-D2000 system is approximately 23 vol% rigid (DGEBA) while the PEGGE2000-PACM system is only 4 vol% rigid (PACM) with similar sized monomers. Therefore, it would be advantageous to have a crystalline diamine cured with DGEBA, allowing a higher fraction of DGEBA in the system. One example of a monomer with potential is low molecular weight amine-terminated polyethylene (PE). PE with molecular weights similar to D2000 are long enough to form crystals having disordered chain ends and a melting point around 124 °C [11]; however, the $T_g$ is $-127$ – $-118$ °C [12] so a significant non-crystalline portion would dramatically reduce the properties. Amine-terminated PE may be difficult to synthesize; however, PEs lightly grafted with maleic anhydride [13] or copolymerized with ethyl acrylate [14] are commercially available so amine functionality should be possible in the modified PEs. These modified PEs retain $T_m$s 100 °C or greater.

### 7.1.4 Glass Bead Reinforcement

The fact that, in many cases, the unfunctionalized glass improved the toughness more than the functionalized glass is interesting and not fully explained. Increased void growth was proposed as the mechanism but the size distribution of the beads made quantifying the void growth to be impossible. Reproducing the tests of Chapter 6 with monodisperse glass beads would allow the void growth to be measured and test that hypothesis. In addition using another type of glass bead could prove to be beneficial.
The beads used in this work were soda-lime. Borosilicate, also known as E glass, has fewer alkali components and a more neutral pH leachate than soda-lime glass [15]; the ASTM epoxy titration may be a valid method for determining the EEW for functionalized borosilicate beads. In addition the beads used in this work had a coating, presumably a sizing package, on the unfunctionalized beads that was undisclosed by the manufacturer. This introduced sulfur and fluorine to the system. Monodisperse, sizing-free beads could verify whether enhanced void growth is the mechanism for the increased toughness using unfunctionalized beads.
List of References


Appendix A: MATLAB Code for FTIR Kinetics

clc
clear T Y k1 k2 sse A B inits E
global k1 k2 inits initial_OH
init_E = 1.475610792; %initial epoxy concentration
start_E = 1.475610792; %epoxy concentration at first FTIR scan
start_PA = 0.737838933; %primary amine concentration at first FTIR scan
start_SA = 0; %secondary amine concentration at first FTIR scan
start_TA = 0;
initial_OH = 0.02*init_E+0.0; %initial hydroxyl concentration

t_span = 2:2:450; %time span of interest - start:interval:end
inits = [start_E start_PA start_SA start_TA];
m = 0;
i = 0;
for k1 = 0.005:0.0001:0.015
    i = i + 1;
    j = 0;
    for k2 = 0.000015:0.00005:0.0025
        j = j + 1;
        [T,Y] = ode15s(@pcr,t_span,inits);
        m = m + 1;
        B(:,:,m) = Y;
        for k = 1:4
            sse(i,j,k) = sum((Y(:,k) - Expr(:,k)).^2);
        end
        E(i,j) = (sse(i,j,1)+sse(i,j,2))/2;
    end
    A(i,j,1) = k1;
    A(i,j,2) = k2;
end
end

[minval,ind] = min(E(:));
\[ [I,J] = \text{ind2sub}([\text{size}(E,1) \ \text{size}(E,2)], \text{ind}); \]
\[ k1 = A(I,J,1) \]
\[ k2 = A(I,J,2) \]

% following code generates a plot of the best fit concentrations and experimental data
\[ [T,Y_{\text{best}}] = \text{ode15s}(\text{@pcr}, \text{t_span}, \text{inits}); \]
figure; plot(T,Y_{\text{best}}(:,1),T,Y_{\text{best}}(:,2),T,Y_{\text{best}}(:,3),T,Y_{\text{best}}(:,4),T,Expr(:,1), '*', T,Expr(:,2), '+', T,Expr(:,3), 'o', T,Expr(:,4), 'x')
xlabel('Time (minutes)')
ylabel('Conc (mol/L)')

% following code plots the error as a function of k1 and k2
figure; contour(A(:,:,1),A(:,:,2),E)
xlabel('k1')
ylabel('k2')

% Additional file (named pcr.m) listing the differential equations called in the above code
function dy = pcr(t,y)
global k1 k2 initial_OH
dy = zeros(4,1); % a column vector
dy(1) = -k1*y(1)*y(2)*(initial_OH+y(3)+2*y(4)) - 
     k2*y(1)*y(3)*(initial_OH+y(3)+2*y(4));
dy(2) = -k1*y(1)*y(2)*(initial_OH+y(3)+2*y(4));
dy(3) = k1*y(1)*y(2)*(initial_OH+y(3)+2*y(4)) - 
     k2*y(1)*y(3)*(initial_OH+y(3)+2*y(4));
dy(4) = k2*y(1)*y(3)*(initial_OH+y(3)+2*y(4));
Appendix B: Frequency Dependence of $T_g$ and $T_\beta$

Figure B.1: $T_\beta$ (left) and main $T_g$ (right) shifts with frequency for D230.
Figure B.2: $T_\beta$ (left) and main $T_g$ (right) shifts with frequency for B270.

Figure B.3: $T_\beta$ and intermediate transitions (left) and main $T_g$ (right) shifts with frequency for B390.
Figure B.4: $T_\beta$ (left) and main $T_g$ (right) shifts with frequency for D400.

Figure B.5: $T_\beta$ and intermediate transitions (left) and main $T_g$ (right) shifts with frequency for B440.
Figure B.6: $T_\beta$ and intermediate transitions (left) and main $T_g$ (right) shifts with frequency for B620.
Figure B.7: $T_g$ shift with temperature for B1000-D230.

Figure B.8: $T_g$ shift with temperature for B1000-D400.
Figure B.9: $T_\beta$ and $T_\gamma$ (left) and main $T_g$ (right) shifts with frequency for D2000.
Appendix C: Fracture Surfaces of Glass-filled Samples

Figure C.1: Microscope images and height profiles for B440: D230 + plGlass: A & B are at 20× while C & D are at 100× magnification.
Figure C.2: Microscope images and height profiles for B440: both + pIGlass: A & B are at 20× while C & D are at 100× magnification.
Figure C.3: Microscope images and height profiles for B440: D2000 + plGlass: A & B are at 20× while C & D are at 100× magnification.
Figure C.4: Microscope images and height profiles for D400 + plGlass: A & B are at 20× while C & D are at 100× magnification.
Figure C.5: Microscope images and height profiles for D400 + epGlass: A & B are at 20× while C & D are at 100× magnification.
Figure C.6: Microscope images and height profiles for B440: D2000 + epGlass: A & B are at 20× while C & D are at 100× magnification.
Figure C.7: Microscope images and height profiles for B440: both + epGlass: A & B are at 20× while C & D are at 100× magnification.
Figure C.8: Microscope images and height profiles for B440: D230 + epGlass: A & B are at 20× while C & D are at 100× magnification.
Figure C.9: Microscope images and height profiles for D400: D2000 + epGlass: A & B are at 20× while C & D are at 100× magnification.
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