Yield behavior and energy absorbing mechanisms of single and multi-phase glassy thermosets subjected to multiaxial stress states.

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YIELD BEHAVIOR AND ENERGY ABSORBING MECHANISMS
OF SINGLE AND MULTI-PHASE GLASSY THERMOSETS
SUBJECTED TO MULTIAXIAL STRESS STATES

A Dissertation Presented
by
ROBERT STEVEN KODY

Submitted to the Graduate School of the
University of Massachusetts Amherst in partial fulfillment
of the requirements for the degree of

DOCTOR OF PHILOSOPHY

February 1999

Department of Polymer Science and Engineering
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ROBERT STEVEN KODY

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Alan J. Lesser, Chair

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ACKNOWLEDGEMENTS

This thesis is not simply the result of four years of dedication and hard work. It is a symbol to what can be accomplished when a young person is given the proper tools and guidance throughout his or her life. And especially it is a tribute to my family, friends, teachers, coworkers, employers and advisors, who have given me the tools and guidance. I would like to thank you all. More importantly, I assure you that your hard work will not go to waste.

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ABSTRACT

YIELD BEHAVIOR AND ENERGY ABSORBING MECHANISMS OF SINGLE AND MULTI-PHASE GLASSY THERMOSETS SUBJECTED TO MULTIAXIAL STRESS STATES

FEBRUARY 1999

ROBERT STEVEN KODY, B.S., UNIVERSITY OF MICHIGAN

PH.D., UNIVERSITY OF MASSACHUSETTS AMHERST

Directed by: Professor Alan L. Lesser

This thesis describes an investigation into the multiaxial yield behavior of single and multi-phase glassy thermosets. Specifically we evaluated the yield behavior of pure, rubber-modified, and voided epoxies, as a function of: molecular architecture, morphology, stress state, strain rate and temperature. This work resulted in: a phenomenological model that incorporates both molecular and testing parameters to describe the full yield behavior of single-phase thermosets, and an improved understanding of the importance of particle cavitation, inelastic void growth and other local irreversibilities in multi-phase materials.

The work on the single and multi-phase epoxy thermosets both began with the design of a biaxial testing facility and a specimen fabrication protocol. Using this testing
facility to test thin-walled hollow cylinders has allowed us to evaluate the yield and brittle failure response of materials in stress states ranging from uniaxial compression to biaxial tension. Two of the challenges involved in developing such a facility were: fabricating well aligned hollow cylinder specimens, and testing samples at a constant strain rate independent of stress state. After meeting these challenges, thin walled hollow cylinders were tested in stress states ranging from uniaxial compression to biaxial tension.

With regard to describing the yield behavior of single-phase glassy thermosets, we investigated the effects of both test conditions and molecular parameters on the yield/deformation behavior. Using these results, a generalized yield model was developed, evaluated and later modified. The model ties both test conditions and molecular parameters to the yield response of glassy polymer networks.

The later chapters of this thesis focus on experimentally investigating the deformation behavior of multi-phase polymer systems and the analytical models that describe their behavior. The hollow cylinder tests were conducted on rubber-modified and voided epoxies, to determine their macroscopic yield/failure envelopes. Models that predict the threshold levels for rubber particle cavitation and the macroscopic yield behavior of a perfectly plastic media containing voids were then evaluated. To study the energy absorbing mechanisms involved with deforming rubber-modified epoxy networks, we also investigated the microstructural changes that occur prior to gross yielding. This was accomplished by loading and unloading hollow cylinders in equi-biaxial tension, and observing changes in hysteresis, loading stiffness, and microstructure. Specifically, we measured both the onset and magnitude of energy dissipation primarily due to irreversible
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CHAPTER 1

INTRODUCTION

1.1 Rational and Relevance

Many of today’s engineering applications require materials to survive multiaxial states of stress and severe environments. In composites, these stresses arise from the confinement imposed by the reinforcement (e.g., rigid particles or fibers). In adhesives, coatings, and electronic encapsulations, multi-axial stresses are generated from the confinements imposed by the substrate and other geometric restrictions. To meet these demands, material suppliers have developed a wide array of engineering thermosets, thermoplastics and composites, of which the properties can be tuned to meet specific applications. This tuning typically involves altering molecular architecture or morphology, by mixing different resins and curing agents, or adding modifiers. Unfortunately the manner in which changing molecular architecture and composite morphology affect the yield behavior is not fully understood. Consequently, there is a need for experimental studies and subsequent analytical models to describe the yield and deformation behavior of single and multi-phase polymers subjected to varying stress states and environments.

A thorough understanding of the deformation behavior of a multiphase system requires: a detailed understanding of the deformation mechanisms of each constituent, a description of the morphology, and an understanding of the interaction between the different constituents. Therefore, in order to understand and model the yield behavior of multi-phase
glassy polymers, one must first understand the yield behavior of the pure single-phase materials alone. To date there have been numerous studies and models that successfully describe the yield behavior of specific glassy polymers under selected loading conditions. However, there are no models that describe the generalized yield behavior of an entire class of polymers as a function of molecular architecture, stress state, strain rate and temperature.

In this thesis, we first review existing yield studies and models that separately describe the effects of molecular architecture, stress state, strain rate, and temperature in single-component glassy polymers. Today, there is no model that can combine all effects to predict yield. Similarly, for multi-phase materials, we review studies and models that attempt to describe the energy absorbing mechanisms and yield behavior of rubber-modified polymers. We then describe our own multiaxial investigation into the generalized yield behavior of both single and multi-phase epoxy based thermosets, which has led to a more complete understanding of the deformation mechanisms and failure criterion of these materials. We develop a phenomenological model to describe the full yield response of single-phase glassy polymers, and critique existing models that describe macroscopic yielding and the energy dissipating micro-mechanisms of rubber-modified and voided epoxy systems.

1.2 Single-Phase Glassy Polymers

Today the use of single phase glassy polymers in engineering applications is more the exception than the rule. Yet before one can truly understand the yield and deformation behavior of multi-phase engineering materials, a full understanding of the yield and failure
behavior of the single-phase constituents must be obtained. To better understand the deformation and yield behavior of one class of materials, glassy polymer networks, we investigated the multiaxial yield behavior of model epoxy based thermosets with systematically controlled molecular architectures. The molecular architecture of an epoxy based thermoset is systematically controlled by altering the molecular weight between crosslinks and curing agents’ stiffness (e.g. aliphatic to aromatic). Thin-walled hollow cylinders were then tested in stress states ranging from uniaxial compression to biaxial tension, as a function of strain rate and temperature. From the experimental results of the pure epoxy, we developed a phenomenological yield model that incorporates the effects of both testing conditions and molecular parameters. This model was developed by generalizing some of the approaches used by past researchers, to develop a single working model that can be modified as we learn more about this class of materials. In fact, the first modification to the model is also presented in this thesis.

1.3 Multi-Phase Glassy Polymers

There are numerous types of multi-phase polymer systems. From the quasi-isotropic carbon-fiber epoxy resin laminate used in high performance aircraft to recycled tire-rubber reinforced asphalt found in America’s highways, the primary purpose of adding a second phase to a polymer system is to improve the mechanical performance. These improvements typically come from the energy absorbing micro-mechanisms discussed above. As such in this thesis, we have attempted not only to evaluate the macroscopic yield
response of rubber-modified and voided epoxy thermosets, but also to relate the yield response to local micro-mechanisms of irreversibility.

Before introducing the work on multi-phase glassy polymers that is described in this thesis, we should first explain how very different these materials are from single-phase systems. For the case of multi-component systems, localized yielding and other microscopic mechanisms of irreversibility are observed well before macroscopic yielding arises. In general, three regimes are possible during the deformation of a multi-phase polymer. This general case is illustrated by the tensile stress-strain response of a rubber-modified epoxy in Figure 1.1. The stress-strain curve has been divided into three regimes to illustrate the state of the material as it is loaded to yield or failure. The regimes can be described as follows:

**Regime I: Linear Elastic/Viscoelastic Regime**

Both components of the material and the interface between them are intact. In this region the composite material behaves linear elastically or viscoelastically. The composite properties (e.g. density, stiffness, etc.) are well described by current micromechanics models\(^1\)\(^-\)\(^3\). Both the bulk and shear modulus of rubber-modified epoxies can be predicted by a model described by Christensen\(^2\).

**Regime II: Localized Yield Regime**

Microscopic irreversibility is evident, but gross yielding is not yet realized. Often one or both components or the interface between them fails, allowing the other component to begin yielding on a microscopic
Figure 1.1: Stress-strain response of pure and rubber-modified epoxy, illustrating the three regions of deformation in a multi-phase material.
level. Much qualitative work, describing the micro-mechanisms of Regime II, has been published in the literature. However, quantitative measurements have been limited to uncontrolled stress states (e.g. fracture toughness tests) or unconfined stress states (e.g. uniaxial tension), and therefore there are no models that incorporate these mechanisms to predict yield. In rubber-modified epoxy, Regime II typically begins with the onset of rubber particle cavitation or debonding, followed by inelastic void growth or localized shear yielding in the epoxy surrounding the cavitated particles; Only localized yielding of the continuous phase is observed.

Regime III: Macroscopic Yield Regime

Gross yielding or failure is evident in all constituents. Irreversible deformation propagates through such a significant amount of material, that effectively the entire sample yields macroscopically. This final regime of macroscopic yield has been well characterized in single-phase materials. However, few models have been proposed to describe this response that incorporate the micro-mechanisms of Regime II. There are currently no models available in the literature that incorporate all of these mechanisms to predict macroscopic yield.

To fully understand the macroscopic yield response of a multi-phase polymer system, one must first understand and model the energy absorbing micro-mechanisms of the individual components, and relate these to the macroscopic response of the material. Along
these lines, Section 2.2 and Chapters 5 and 6 of this thesis attempt to describe how the microscopic energy absorbing mechanisms affect the macroscopic deformation and yield response of rubber-modified and voided epoxy thermosets. The voided epoxies could prove to be most useful, because the local irreversibility of the matrix is completely deconvoluted from any rubbery inclusion.

The multi-phase materials were tested over a range of stress states to evaluate how the energy absorbing mechanisms and the yield/failure behavior change with stress state. The multi-phase systems were made by adding a second phase of CTBN rubber or gaseous hexane or propylbenzene voids to the epoxy. Fracture toughness tests were run to qualitatively identify the energy absorbing micro-mechanisms of the multi-phase materials. Then biaxial testing was used in combination with scanning electron microscopy (SEM) to determine the onset of rubber particle cavitation and irreversible matrix deformation, in more controlled loading conditions. Finally, the macroscopic yield envelopes were measured and compared with existing models.
CHAPTER 2

BACKGROUND

2.1 Yield Behavior of Single-Phase Glassy Polymers

2.1.1 Effect of Molecular architecture

To date a complete understanding of how the yield strength of glassy thermosets is affected by molecular architecture is not available, as studies on the effect of intrinsic material characteristics (e.g. $M_c$; glass transition temperature, $T_g$; chain stiffness; etc.) are limited. One goal of this work is to investigate the relationship between molecular architecture and material properties. Epoxy based thermosets are ideal for this due to the accuracy with which the molecular weight between crosslinks, $M_c$, and backbone stiffness can be controlled.

Of the components that make up molecular architecture, only the effect of $M_c$ has been studied thoroughly\textsuperscript{4,5}. Specifically yield strength, $\sigma_y$, has been shown to increase linearly with $\frac{1}{M_c}$\textsuperscript{6}. Similarly, Bradley\textsuperscript{7} showed that for a variety of epoxy networks, $\sigma_y$ also increases linearly with $T_g$. We have also found such a relation between $\sigma_y$ and $T_g$, which can be described by the following equation:

$$\sigma_y = \sigma_y^T + \alpha (T - T_g) \quad \text{for } T<T_g \quad (2.1)$$
where $\sigma_y^{T_s}$ represents the yield stress at $T_g$, and $\alpha$ is a negative term that describes the linear increase in $\sigma_y$ as $T$ is decreased below $T_g$.

As $\sigma_y$ increases linearly with both $\frac{1}{M_c}$ and $T_g$, a linear relationship between $T_g$ and $\frac{1}{M_c}$ is expected. In 1955, Fox argued that $T_g$ should increase in a linear fashion with $\frac{1}{M_c}$ due to the decrease in conformational entropy:

$$T_g = T_{g0} + \frac{\phi}{M_c} \quad (2.2)$$

where $T_{g0}$ is the glass transition temperature of a linear polymer and $\phi$ is an empirical constant describing the increase in $T_g$ as $M_c$ is decreased. This was found to be true for a number of polymers, and a universal constant of $\phi = 39$ K kg/mol was proposed by Nielson. Later, Fisher showed that the value of $\phi$ is strongly affected by the backbone stiffness of the resin and curing agents and can range between 7 and 55 K kg/mol for most commercial systems. More recent studies by Crawford and Lesser have shown that the functionality of the crosslink also affects the value of $\phi$. Therefore, by understanding how molecular architecture affects $T_{g0}$ and $\phi$ in equation (2.2), equation (2.1) should describe the effect of molecular architecture on $\sigma_y$ for a glassy thermoset. Note that equation (2.1) is only valid if the stress state and strain rate are unchanged.
2.1.2 Effect of Stress State, Strain Rate, and Temperature

The understanding of yield behavior of glassy polymers took a leap forward in the late 1960’s. In this period, experiments began to show that the yield strength of several glassy polymers was dependent on the state of stress. These findings are consistent with every relevant study to date; Polymers exhibit a significant decrease in yield strength with increasing hydrostatic component of stress, \( \sigma_m \). For this reason, any yield criterion for glassy polymers must include the effect of \( \sigma_m \).

One of the early criteria proposed to describe the yielding of glassy polymers in different stress states was a modified Tresca criterion shown as:

\[
\tau_y = \tau_{y0} - \mu \sigma_m
\]

(2.3)

where \( \tau_y \) is the maximum shear yield stress, \( \tau_{y0} \) is the shear yield stress in the absence of hydrostatic stress, and \( \mu \) is the coefficient of internal friction. Bowden\(^{18}\) proposed this criterion in 1968 to describe the yield response of poly(methylmethacrylate) (PMMA) and poly(ethylene terephthalate) (PET). He measured the tensile yield stress while applying a transverse compressive load. This test can only investigate stress states ranging from uniaxial compression to uniaxial tension and suffers from frictional effects due to the transverse load. Despite these limitations, this model has been shown to fit the yield response of several polymers, reasonably well\(^{12, 14, 20}\). Unfortunately in these studies, multiple sample geometries were often used to arrive at the different stress states. This approach limits the number of different stress states that can be investigated and convolutes the results with effects of fabricating different specimen geometries.
In 1969, Sternstein and Ongchin\textsuperscript{10} showed that the yield behavior of PMMA more closely follows a modified von Mises criterion described below:

\[ \tau_{y}^{\text{oct}} = \tau_{y0}^{\text{oct}} - \mu \sigma_m \]  

(2.4)

where \( \tau_{y}^{\text{oct}} \) is the shear yield stress along the octahedral plane, and \( \tau_{y0}^{\text{oct}} \) is the octahedral shear yield stress in the absence of \( \sigma_m \). The pressurized thin walled hollow cylinder specimen geometry, that Sternstein used, allows a single specimen geometry to continuously investigate stress states ranging from uniaxial compression to biaxial tension. Subsequent studies have shown that equation (2.4) generally describes the yield response of other glassy polymers, including thermosets\textsuperscript{11,13-15}.

Most relevant with regard to epoxies, Sultan and McGarry\textsuperscript{11} showed that equation (2.4) generally describes the yield response of epoxy networks. For the case of a diglycidyl ether of bis-phenol A (DGEBA) cured with Shell Corporation’s curing agent D, they obtained values of \( \tau_{y0}^{\text{oct}} = 39\text{MPa} \) and \( \mu = 0.175 \). No mention of the effects of strain rate, temperature or molecular architecture on \( \tau_{y0}^{\text{oct}} \) and \( \mu \) was made. In 1983, Kinloch\textsuperscript{24} summarized the reported values of \( \tau_{y0}^{\text{oct}} \) and \( \mu \) for several different polymers and stated that, in general, \( \tau_{y0}^{\text{oct}} \) and \( \mu \) would be affected by changes in strain rate and temperature, but presented no data to suggest how these parameters might change. Despite these predictions, no study fully considered the viscoelastic response of the materials. Therefore, Sternstein’s model and its application remain primarily phenomenological, and with recent exception\textsuperscript{23}, little attempt has been made to determine how molecular architecture, strain rate, and
temperature affects $\tau_{yo}^\mathrm{ext}$ and $\mu$. Consequently, direct application of equation (2.4) has been severely hindered.

Other efforts have concentrated on describing the effects of test temperature and strain rate on the yield response of polymers. In 1966, Robertson\textsuperscript{25} considered that the yield response of glassy polymers is governed by intramolecular forces. He described shear yielding as a thermally activated process whereby the backbone of a molecule is transformed from a low energy, *trans* conformation to a higher energy, *gauche* conformation. The final form of Robertson's model reduces to an Eyring\textsuperscript{26} type model. Ward et al.\textsuperscript{12} extended Robertson's model to include the effects of hydrostatic stress. Ward considered that the molecular transformation from a *trans* to a *gauche* conformation implies a reduction in density due to less efficient packing, which produces an interaction with the hydrostatic component of the applied stress. Ward's model takes the following form:

$$\dot{\gamma} = \Gamma \exp \left( - \frac{\Delta E - \tau_y \nu + p\Omega}{RT} \right) \quad (2.5)$$

where: $\dot{\gamma}$ is the shear strain rate

$\Delta E$ is the activation energy

$\tau_y$ is the shear yield stress

$p$ is the hydrostatic pressure (positive $p$ denotes hydrostatic compression)

$\nu$ and $\Omega$ are the activation volumes for shear and hydrostatic flow, respectively

$R$ is the Gas constant

$T$ is the absolute temperature

$\Gamma$ is a proportionality constant.
Ward showed that equation (2.5) could describe the difference in yield behavior measured between uniaxial tension and compression in addition to the strain rate and temperature effects in PET and PMMA.

Two additional theories worth noting which are based upon physical descriptions of plastic flow of yield on a molecular level have been developed by Bowden\textsuperscript{27} and Argon\textsuperscript{14}. The Bowden and Argon theories, which are different from each other in approach, are both concerned with the thermal activation of molecular displacements that take place during plastic flow. Argon's theory considers that yielding occurs via the thermally activated production of molecular kinks which they modeled by the formation of wedge disclinations. This theory includes the effect of hydrostatic stresses and has successfully modeled the yield behavior of a number of glassy polymers including polystyrene, PMMA, PET and polycarbonate\textsuperscript{14,28}. However, more recent attempts to apply Argon's theory to epoxy resins cured with triethylenetetramine showed agreement only at the lower temperatures\textsuperscript{29}.

Bowden's theory\textsuperscript{27} considers that the critical step in the yield of a polymer glass is a thermally activated nucleation of small disc-shaped shear regions in the polymer whereby the strain fields produced by these regions could be modeled using a Burger's vector. Young showed that this model accurately predicts the rate and temperature response of epoxies over a broader temperature range than that predicted by Argon's model\textsuperscript{29}. However, Bowden's model does not account for changes in the yield stress as the hydrostatic stresses are changed.
2.2 Deformation and Yield Behavior of Multi-Phase Glassy Polymers

2.2.1 Energy Absorbing Micro-mechanisms

It is well established that a primary toughening mechanism in many rubber-modified polymeric materials involves the relief of hydrostatic stress through rubber particle cavitation or debonding, followed by inelastic void growth in the matrix material\textsuperscript{30,31}. This process has been reported in rubber toughened epoxies\textsuperscript{32,33}, showing that both rubber particle cavitation and inelastic void growth are primary toughening mechanisms in highly confined stress states.

Of these two mechanisms, rubber particle cavitation has received the most attention in the literature. Early work by others has indicated that the cavitation strength of bulk rubber scales its shear modulus\textsuperscript{64-66}. However, concerns are raised with regard to using their estimates to predict cavitation in small particles since their results incorporate the assumption of flaws are on the order of the particle size. More recent work has shown that two parameters reported to control the effectiveness of cavitation are particle size and modifier surface energy\textsuperscript{11,31,34-40}. Earlier studies have shown that rubber particles exhibit an increased resistance to cavitation as particle size is decreased. The scale-effect in the cavitation resistance has been recently modeled by Lazzeri and Bucknall\textsuperscript{34}, and Dompas and Groeninckx\textsuperscript{31}. Both models are based on energy balance principles and consider that the energy available to produce cavitation is the volumetric strain energy stored in the rubber particle, $U_0$, given by:

$$U_0 = \frac{2}{3} \pi R^3 K_r \varepsilon_v^2$$  \hspace{1cm} (2.6)
where $R$ is the initial particle radius, $K_r$ is the Bulk Modulus of the rubber, and $\varepsilon_v = \varepsilon_{in}$ is volumetric strain. The total energy in the particle after cavitation occurs, $U_C$, is related to the surface energy and cavitation/debond surface area. $U_C$ for the Lazzeri-Bucknall model is given by equation (2.7), and for the Dompas-Groeninekx model by equation (2.8).

$$U_C = \frac{2}{3} \pi K_r R^3 \left( \varepsilon_v - \frac{r^3}{R^3} \right)^2 + 4\pi r^2 \Gamma + 2\pi r^3 G_r \rho \int f(\lambda_t)$$  \hspace{1cm} (2.7)

$$U_C = 4\pi r^2 \Gamma$$  \hspace{1cm} (2.8)

where $r$ is the radius of the cavitated void

- $\Gamma$ is the surface energy of the rubber
- $G_r$ is the shear modulus of the rubber
- $\rho$ represents the density ratio of the rubber before and after cavitation, taken equal to 1
- $f(\lambda_t)$ is a numerical integration of the shear strain function of the rubber after cavitation, taken to be equal to 1.

In both models, the necessary condition for particle cavitation occurs when:

$$U_C \leq U_0$$  \hspace{1cm} (2.9)

For the case of the Dompas-Groeninekx model, the radius of the cavitated surface is calculated by assuming that all of the volume strain in the rubber particle is released upon cavitation (i.e., $r = (\varepsilon_v)^{1/3} R$). The relationship between $r$ and $R$, together with the necessary condition for cavitation (equation 2.9), yields a "scale effect" for rubber particle cavitation where the larger particles cavitate at lower volume strains than the smaller particles. For the Dompas-Groeninekx model this reduces to:
Equation 2.10 defines a critical particle size, $R$, below which cavitation will not occur for a given $\Gamma$, $K_r$, and $\varepsilon_v$. A similar condition can be arrived at using Lazzeri-Bucknall model with the primary difference between the two models being that Lazzeri and Bucknall include the shear energy and residual volumetric energy stored in the rubber particle after cavitation. For uncrosslinked rubber particles with the reported values\textsuperscript{31} of $G_r=0.4$ MPa, $K_r=2$ GPa, and $\Gamma=0.03$ Jm\textsuperscript{-2}, both models are plotted in Figure 2.1, showing the smallest cavitated rubber particle for a given $\varepsilon_v$. Again, both models predict the experimentally observed trend; larger particles cavitate at lower volume strains\textsuperscript{11, 31, 35, 37, 39}.

Additional studies have shown that toughness increases with decreasing particle size down to a minimum critical size, below which the particles do not cavitate and little apparent toughening is realized. However, if particle cavitation does occur, the higher toughness measured for the smaller particles is attributed to the inter-particle distance, which describes the size of a ligament between voids after cavitation. If the size of the ligaments is small enough, then the entire ligament may be able to yield upon cavitation. The effect of inter-particle distance on toughening has been discussed by others\textsuperscript{31, 35, 37, 39, 41-44} and is closely related to inelastic deformation of the matrix material.

It should be noted that other related studies by Farris and Vratsanos have also indicated a that a scale effect in particle size can occur if particle debonding is considered\textsuperscript{67}.

The unique difference between the work presented by Farris and Vratsanos is that they

\[
R = \frac{6\Gamma}{K_r\varepsilon_v^{4/3}} \tag{2.10}
\]
Figure 2.1 The predicted minimum cavitated particle radius versus volumetric strain, for rubber particles with $K_r=2$GPa, $G_r=0.4$MPa, and $G_r=0.03$Jm$^{-2}$. The solid and dashed lines represent the Lazzeri-Bucknall$^{34}$ and Dompas-Groeninckx$^{31}$ cavitation models respectively.
consider overall stiffness change in the modified polymer can be modeled through the addition of voids introduced via particle debonding.

### 2.2.2 Yield/Failure Envelope Predictions

The role of inelastic matrix deformation, usually occurs in the form of shear bands, dilatation bands and inelastic void growth. Unfortunately, models that incorporate their contribution in the macroscopic yield response have been scarce in the literature. Until recently\textsuperscript{34, 38, 45}, the literature has been absent of models that predict the yield response of rubber-modified polymers in arbitrary stress states, whereby cavitation and inelastic void growth are considered.

In 1993 Lazzeri and Bucknall\textsuperscript{34} made a first attempt at introducing a yield criterion for rubber-modified polymers by considering how the polymer matrix would behave macroscopically after some fraction of particles cavitate and effectively act as voids. They extended a theory proposed by Gurson\textsuperscript{46} for a perfectly plastic, von Mises material containing voids, to include the effect of hydrostatic stress on the polymer yield behavior by incorporating a coefficient of internal friction, $\mu_e$. Lazzeri and Bucknall’s yield function, $\Phi$, was introduced as:

$$\Phi = \left(\frac{\sigma_e}{\sigma_0}\right)^2 + \frac{\mu_e \sigma_m}{\sigma_0} \left(2 - \frac{\mu_e \sigma_m}{\sigma_0}\right) + 2f \cosh\left(\frac{3\sigma_m}{2\sigma_0}\right) - f^2 - 1 = 0 \quad (2.11)$$

where: $\sigma_e$ is the von Mises equivalent stress, $\sigma_0$ is the yield stress in the absence of hydrostatic stress, $\sigma_m$ is hydrostatic stress, $\mu_e$ is the tensile equivalent coefficient of internal friction, where $\mu_e = \frac{3}{\sqrt{2}} \mu$, $f$ is the volume fraction of pores dispersed in the
matrix. An equation that incorporates the intrinsic pressure dependence of polymer yield into Gurson’s model has also been proposed by Steenbrink and Van Der Giessen. Both equations predict similar relationships in practice.

Figure 2.2 shows how the yield strength of a perfectly plastic modified von Mises materials, with $\mu_c=0.39$ and $f=0, 0.1, 0.2$ and 0.3, is affect by stress state according to equation (2.11). If all of the rubber particles were to cavitate before yield, one could use the volume fraction of rubber particles for $f$ in equation (2.11) to predict the yield envelope of rubber toughened polymers. Although it should be noted that, at negative hydrostatic stress levels, the particles will not cavitate and may take significant hydrostatic loads. Hence, equation (2.11) should predict a lower bound in this regime, since the model assumes that voids are present as opposed to rubber particles. Under this condition, equation (2.11) would approximate inelastic void collapse to be unbounded in a fashion analogous to inelastic void growth. More directly, equation (2.11) could also be used to predict the yield envelope of voided material with a volume fraction of voids equal to $f$.

### 2.2.3 Debate on the Equivalence of Microvoids and Rubber Particles

As stated in Section 2.2.1, it is well established that a primary toughening mechanism in many rubber-modified polymeric materials involves the relief of hydrostatic stress through rubber particle cavitation or debonding, followed by inelastic void growth in the matrix material. However the relative importance of particle cavitation and inelastic void growth has been the subject of much controversy.
Figure 2.2: Lazzeri-Bucknall yield function predictions (equation 2.11) for a material with $\mu_c = 0.39$ and containing $f = 0.0$, $0.1$, $0.2$ and $0.3$ voids by volume. The solid lines represent Lazzeri-Bucknall model predictions and the dashed lines represent the loading paths in uniaxial compression, pure shear, uniaxial tension, biaxial tension and a plain strain crack tip.

Some authors have suggested that similar toughness could be achieved in toughened plastics by replacing the rubber particles with microvoids. Their work has shown that
polycarbonate with 20% voids by volume\textsuperscript{47} and epoxies modified with hollow latex particles\textsuperscript{39}, precavitated rubber particles\textsuperscript{48}, and non-adhering particles\textsuperscript{49} have a significantly higher fracture toughness than the solid materials. These results suggest that rubber particle cavitation does not significantly contribute to the overall energy absorption in itself, and that the primary role of the rubber particles is simply to nucleate a void. The voids then relieve the hydrostatic stress and dissipate energy through inelastic matrix deformation.

Others believe that these findings are the exception rather than the rule, and that voids weaken and embrittle most glassy polymers\textsuperscript{50,51}. With regard to this second viewpoint, it has been proposed that rubber particles play a very important role in the toughening of polymers, in addition to cavitating. In fact it has been proposed that the particles must remain intact until the local stress level exceeds the yield stress of the matrix, so that shear yielding occurs in the matrix rather than fracture. Following the same line of thought, as a voided material is loaded, the local stress would first reach the brittle strength of the matrix. Hence the material would fracture before matrix yielding could occur. Contradictory to this argument, Guild and Young\textsuperscript{50} have shown using finite element analysis, that the stress concentrator in the matrix material is the same in the presence of a void as it is in the presence of a rubber particle. Additionally, this argument assumes that when a material is loaded above both its yield and brittle strengths, that yielding is the preferred deformation mechanism. This would be surprising, as we expect that the lower of the two strengths would be the preferred failure/deformation mechanism. Regardless of which viewpoint is correct, it is generally agreed that in toughen polymers, the majority of energy dissipation occurs through inelastic matrix deformation, as discussed in Section 2.2.2.
CHAPTER 3

EXPERIMENTAL

3.1 Morphological Study

To examine morphology, samples were first cryo-fractured in liquid nitrogen. The samples were then coated with gold palladium and examined in a JEOL 35CF scanning electron microscope (SEM) in secondary electron imaging (SEI) mode. To measure rubber particle size and volume fraction in the rubber-modified materials, the fractured surfaces were first: stained in a 2% solution of osmiumtetroxide in tetrahydrofuran for 90 minutes, microtomed at room temperature and coated with a light layer of gold palladium, before examination in a JEOL 6320FXV Field Emission SEM in SEI mode. In order to only view the rubber particles at the microtomed surface, the images of the stain rubber-modified epoxy were taken at 3 kV. This low voltage reduces the resolution of the images, making it difficult to determine the precise volume fraction of rubber particles. The average size and volume fraction of voids in the voided epoxies were measured in a JEOL 35CF scanning electron microscope (SEM) in secondary electron imaging (SEI) mode. For both the rubber-modified and voided materials, the average particle/void sizes and concentrations were calculated from the SEM images using quantitative stereology, and are reported in the sections that follow.
3.2 Materials

3.2.1 Controlling Molecular Architecture of the Single-Phase Epoxies

The materials were chosen for accurate control of molecular architecture. The structure and properties of the resins and curing agents used are shown in Table 3.1. To test the effects of a change in backbone structure, a diglycidyl ether of bisphenol A (DGEBA) is reacted with either of two different curing agents systems: one aliphatic and the other aromatic. Please note that a third curing agent, 1-(2-Aminoethyl)piperazine (AEP), was used only in the voided epoxies. Two DGEBA’s were used in this study: one with a narrow molecular weight distribution (EPON 825) and one with a broad molecular weight distribution (EPON 828). The aliphatic curing agents were ethylenediamine (EDA), methylethylenediamine (MEDA) and N,N’-dimethylethylenediamine (DMEDA). EDA and MEDA behave as crosslinking agents, while DMEDA is a chain extender. The MEDA and DMEDA were purchase in a solution containing 85% DMEDA and 15% MEDA by weight. In the remainder of this thesis, we will refer to this curing agent solution as MEDA/DMEDA. For the aromatic epoxies, 1,3-phenylenediamine(MPDA) and aniline are the crosslinker and chain extender, respectively. The similarity of the backbone structures within each curing agent system assures that the polymer backbone stiffness is not significantly altered by changing $M_c$; Backbone structure is only significantly altered by changing curing agent systems. A description of each of the single-phase epoxy materials used in this study is given in Table 3.2. Also the molecular weight between crosslinks for each of the materials is indicated in the appropriate figures.
Table 3.1: Structure and properties of resins and curing agents.

<table>
<thead>
<tr>
<th>Chemical Name</th>
<th>Structure</th>
<th>Functionality</th>
<th>$M_w$ (g/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diglycidyl Ether of Bis-phenol A (DGEBA) (Shell EPON825)</td>
<td><img src="image1" alt="Structure" /></td>
<td>2</td>
<td>344 to 356</td>
</tr>
<tr>
<td>(Shell EPON 828)</td>
<td><img src="image2" alt="Structure" /></td>
<td>2</td>
<td>370 to 384</td>
</tr>
<tr>
<td>1,3-Phenylenediamine (MPDA)</td>
<td><img src="image3" alt="Structure" /></td>
<td>4</td>
<td>108.1</td>
</tr>
<tr>
<td>Aniline</td>
<td><img src="image4" alt="Structure" /></td>
<td>2</td>
<td>93.3</td>
</tr>
<tr>
<td>Ethylenediamine (EDA)</td>
<td><img src="image5" alt="Structure" /></td>
<td>4</td>
<td>60</td>
</tr>
<tr>
<td>N-Methylethylenediamine (MEDA)</td>
<td><img src="image6" alt="Structure" /></td>
<td>3</td>
<td>74</td>
</tr>
<tr>
<td>N, N'-Dimethylethylenediamine (DMEDA)</td>
<td><img src="image7" alt="Structure" /></td>
<td>2</td>
<td>88</td>
</tr>
<tr>
<td>1-(2-Aminoethyl)piperazine</td>
<td><img src="image8" alt="Structure" /></td>
<td>3</td>
<td>129.2</td>
</tr>
</tbody>
</table>
Table 3.2: Description of Single-Phase Epoxies Used in This Study

<table>
<thead>
<tr>
<th>Material Designation</th>
<th>Curing Agents Used (% reacted with epoxide)</th>
<th>( M_c ) (grams/mol)</th>
<th>( T_g ) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aliphatic 380</td>
<td>100% EDA</td>
<td>380</td>
<td>146.0</td>
</tr>
<tr>
<td>Aliphatic 480</td>
<td>75% EDA/25% MEDA/DMEDA</td>
<td>480</td>
<td>114.4</td>
</tr>
<tr>
<td>Aliphatic 380</td>
<td>50% EDA/50% MEDA/DMEDA</td>
<td>640</td>
<td>93.2</td>
</tr>
<tr>
<td>Aliphatic 380</td>
<td>25% EDA/75% MEDA/DMEDA</td>
<td>950</td>
<td>73.9</td>
</tr>
<tr>
<td>Aliphatic 380</td>
<td>100% MEDA/DMEDA</td>
<td>1790</td>
<td>66.3</td>
</tr>
<tr>
<td>Aromatic 430</td>
<td>100% MPDA</td>
<td>430</td>
<td>168.1</td>
</tr>
<tr>
<td>Aromatic 680</td>
<td>75% MPDA/25% Aniline</td>
<td>680</td>
<td>143.2</td>
</tr>
<tr>
<td>Aromatic 900</td>
<td>50% MPDA/50% Aniline</td>
<td>900</td>
<td>121.8</td>
</tr>
<tr>
<td>Aromatic 1840</td>
<td>25% MPDA/75% Aniline</td>
<td>1840</td>
<td>108.7</td>
</tr>
</tbody>
</table>
Calculations for $M_c$ were made using the following equation:

$$M_c = \frac{2 \left( M_c + \sum_{f=2}^{\infty} \frac{M_f}{\Phi_f} \right)}{\sum_{f=3}^{\infty} (\Phi_f)}$$

where $f$ functionality of amine

$M_f$ molecular weight of $f^{th}$ functional amine

$M_e$ epoxide equivalent weight (grams of resin per mole of epoxide)

$\Phi_f$ mole fraction of amine hydrogens provided by $f^{th}$ functional amine.

Full details on the method used to calculate $M_c$ are in the paper by Crawford and Lesser\textsuperscript{9}.

### 3.2.2 Controlling the Morphology of the Rubber-Modified Epoxies

The rubber modified epoxy used in this investigation was made from a diglycidyl ether of bisphenol A (DGEBA), reacted with 0%, 10%, and 20% end functionalized carboxyl terminated butadiene acrylonitrile rubber (CTBN 1300X8) by weight, and then cured with aromatic amines. The DGEBA, supplied by Shell Chemical Company (EPON 828), was reacted with the CTBN rubber by mixing the two at 140°C for 4 hours. The structure and molecular parameters of the CTBN rubber is described in Table 3.3. This process and the properties of CTBN rubber are described elsewhere\textsuperscript{39, 43}. The rubber-modified epoxy was then cured with stiochiometric amounts of 1,3-phenylenediamine (MPDA) and Aniline, such that 50% of the epoxide groups reacted with MPDA and 50% reacted with Aniline. These materials were then spun-cast at either 50°C or ~100°C to form thin-walled hollow cylinders with different particle sizes. Spinning at ~100°C resulted in a lower viscosity pre-cured resin and hence significantly larger and bi-modal population of
rubber particles. After gelation, the epoxy was post-cured at 150°C for 3 hours, and slow cooled in the oven. Using this procedure, all samples were made with a calculated molecular weight between crosslinks of $M_c = 900$ grams/mol. Details on the method used to calculate $M_c$ can be found elsewhere. Four different resin formulations were studied to investigate the effects of particle size and concentration. These resins are described in Table 3.4. SEM images showing particle sizes in each of the materials is shown in Figure 3.1. Since the volume fraction of rubber particles is significantly higher than the volume fraction of CTBN rubber added to the hollow cylinder samples, it is probably that there is epoxy resin inside of the rubber particles.

<table>
<thead>
<tr>
<th>Chemical Name</th>
<th>Functionality</th>
<th>$M_w$ (grams/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexane</td>
<td>no reaction</td>
<td>69.0</td>
</tr>
<tr>
<td>Propylbenzene</td>
<td>no reaction</td>
<td>120.2</td>
</tr>
<tr>
<td>Carboxyl-terminated butadiene-acrylonitrile rubber(CTBN1300X8)</td>
<td>2</td>
<td>4200</td>
</tr>
</tbody>
</table>

Table 3.3: Structures and molecular parameters of modifiers.
Table 3.4: Description of Rubber-Modified Epoxies

<table>
<thead>
<tr>
<th>Material Designation</th>
<th>$M_c$ (grams/mol)</th>
<th>Rubber Concentration (weight %)</th>
<th>Particle Concentration (volume %)</th>
<th>Mean Particle Diameter (µm)</th>
<th>$T_g$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>900</td>
<td>0</td>
<td>0</td>
<td>not applicable</td>
<td>124</td>
</tr>
<tr>
<td>B</td>
<td>900</td>
<td>10</td>
<td>13</td>
<td>$1.7 \pm 1.3$</td>
<td>122</td>
</tr>
<tr>
<td>C</td>
<td>900</td>
<td>20</td>
<td>29</td>
<td>$2.3 \pm 0.8$</td>
<td>119</td>
</tr>
<tr>
<td>D</td>
<td>900</td>
<td>20</td>
<td>25</td>
<td>$3.1 \pm 2.5$</td>
<td>119</td>
</tr>
</tbody>
</table>
Figure 3.1: 3kV SEI SEM micrographs of the rubber modified hollow cylinders that have been cryofractured, liquid stained with osmiumtetroxide, microtomed, and gold coated. 3.1a) samples B, 3.1b) samples C, and 3.1d) samples D.
3.2.3 Controlling the Morphology of the Voided Epoxies

The method used to make the materials for this study follows closely to that recently reported by Kiefer, Hilborn and Hedrick\textsuperscript{52}, in which they chemically induced phase separation between a low molecular weight solvent and the epoxy before curing. Two types of voided epoxies were fabricated for this investigation: a hexane-modified epoxy and a propylbenzene-modified epoxy. The hexane-modified epoxy was made by reacting EPON 825 with a stoichiometric amount of 1-(2-Aminoethyl)piperazine (AEP), and the propylbenzene-modified epoxy was made by reacting EPON 828 with a stoichiometric amount of AEP.

For both materials, the resin was maintained at 45°C prior to mixing with the AEP. After mixing the resin with the AEP, the solvent was added to the beaker. The amount of solvent added to the resin, along with the properties of the materials are given in Table 3.5. Note in Table 3.5 that the reported amount of solvent added to the resin represents the percent by weight of solvent, relative to the entire solution (the resin, the AEP and the solvent combined). The resin, curing agent and solvent were then mixed together with a stir bar for several minutes. The mixture was degassed in a vacuum oven, and either poured into a stainless steel tube to make thin walled hollow cylinders, poured into a 3/8 inch inner diameter test tube to make compression specimens, or it was poured between glass plates to make 1/4 inch thick plaques for fracture specimens. The curing of these materials typically involved three stages. The temperatures and length of each stage is given in Table 3.6.

In the first stage, the stainless steel tubes were spun in an oven and the test tubes and plaques were placed in an oven to gel. It is this first stage that predominately determines the
Table 3.5: Description of voided and swelled epoxies.

<table>
<thead>
<tr>
<th>Material Description</th>
<th>Material Description</th>
<th>$M_c$ (g/mol)</th>
<th>$T_g$ (°C)</th>
<th>solvent weight % (wt%)</th>
<th>% voids (vol %)</th>
<th>Mean Void Diameter (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EPON 825-AEP w/ 0% solvent</td>
<td>440</td>
<td>126</td>
<td>0</td>
<td>0</td>
<td>N/A</td>
<td></td>
</tr>
<tr>
<td>EPON 825-AEP w/ 17wt% Hexane</td>
<td>440</td>
<td>93</td>
<td>20</td>
<td>7</td>
<td>not recorded</td>
<td></td>
</tr>
<tr>
<td>EPON 825-AEP w/ 17wt% Hexane (hollow cylinders)</td>
<td>440</td>
<td>93</td>
<td>20</td>
<td>4</td>
<td>5.0 ± 3.3</td>
<td></td>
</tr>
<tr>
<td>EPON 828-AEP w/ 0% solvent</td>
<td>460</td>
<td>128</td>
<td>17</td>
<td>0</td>
<td>N/A</td>
<td></td>
</tr>
<tr>
<td>EPON 828-AEP w/ 29wt% propylbenzene</td>
<td>460</td>
<td>58</td>
<td>29</td>
<td>28</td>
<td>3.6 ± 1.1</td>
<td></td>
</tr>
<tr>
<td>EPON 828-AEP w/ 29wt% propylbenzene</td>
<td>460</td>
<td>52</td>
<td>29</td>
<td>32</td>
<td>4.7 ± 1.2</td>
<td></td>
</tr>
<tr>
<td>EPON 828-AEP w/ varying wt% propylbenzene</td>
<td>460</td>
<td>48-53</td>
<td>See</td>
<td>See</td>
<td>See</td>
<td>Figure 3.3</td>
</tr>
<tr>
<td>EPON 828-AEP w/ varying wt% propylbenzene</td>
<td>460</td>
<td>48-53</td>
<td>varied</td>
<td>0</td>
<td>N/A</td>
<td></td>
</tr>
</tbody>
</table>
Table 3.6: Description of the cure stages for voided and swelled epoxies.

<table>
<thead>
<tr>
<th>Material Description</th>
<th>Stage 1 (°C/hours)</th>
<th>Stage 2 (°C/hours)</th>
<th>Stage 3 (°C/hours)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EPON 825-AEP w/ 0% solvent</td>
<td>21/24</td>
<td>50/2</td>
<td>150/2</td>
</tr>
<tr>
<td>EPON 825-AEP w/ 17wt% Hexane (voided fracture specimen and hollow cylinders)</td>
<td>21/24</td>
<td>50/2</td>
<td>150/2</td>
</tr>
<tr>
<td>EPON 828-AEP w/ 0% solvent</td>
<td>21/24</td>
<td>130/2</td>
<td>160/1</td>
</tr>
<tr>
<td>EPON 828-AEP w/ 29wt% propylbenzene (voided hollow cylinders)</td>
<td>45/24</td>
<td>130/2</td>
<td>160/0.5</td>
</tr>
<tr>
<td>EPON 828-AEP w/ 29wt% propylbenzene (voided fracture specimen)</td>
<td>45/24</td>
<td>130/2</td>
<td>160/1</td>
</tr>
<tr>
<td>EPON 828-AEP w/ varying wt% propylbenzene (voided compression bullets)</td>
<td>21 or 45 /24</td>
<td>130/2</td>
<td>150/1</td>
</tr>
<tr>
<td>EPON 828-AEP w/ varying wt% propylbenzene (swelled/non-voided all samples)</td>
<td>45 or 80 /24</td>
<td>130/2</td>
<td>150/1</td>
</tr>
</tbody>
</table>
morphological structure of the material. The temperature at which the samples were gelled in the first stage depends on the percentage of solvent in the resin, the type of solvent, and the desired morphology. Typically to make voided epoxies, large quantities of solvent are added to the resin and the samples are gelled at relatively low temperature. This causes the solvent to phase separate from the epoxy as the molecular weight of the network increases. At the end of this stage, the phase separated samples become opaque, as the phase separated solvent forms liquid spherical inclusions in the epoxy. To make swelled epoxies, typically smaller quantities of solvent are added to the resin and the samples are gelled at higher temperatures, so the solvent remains in the epoxy as the molecular weight of the network increases.

In the second cure stage, the crosslink density of the epoxy network continues to increase, but the cure temperature does not exceed the boiling temperature of the solvent. In the third and final post cure, the reaction between the epoxy resin and the AEP curing agent reaches full conversion. In the swelled materials, the cure temperature is kept below the boiling temperature of the solvent to suppress phase separation. In the phase separated materials, the cure temperature in this third stage is elevated above the boiling point of the solvent. This causes the solvent domains to evaporate, forcing the solvent into the epoxy matrix and also evaporating it out of the sample. This third stage leaves a swelled, but voided epoxy material. Consequently, the glass transition, $T_g$, of the matrix material is suppressed by the residual solvent. Note that for the compression bullets with a low volume fraction of voids, the final cure temperature was not raised above the boiling point of the propylbenzene, because the phase change of the excess residual solvent would cause the
swelled samples to fracture. As stated previously, the resulting voided and swelled materials are described in Table 3.5. The SEM micrographs of the voided materials that were used for the hollow cylinder and fracture testing are shown in Figure 3.2. The SEM micrographs, along with the volume fraction of voids($f$), weight percent propylbenzene added, $T_g$'s, and particle size distributions of the voided samples used in the compression tests are shown in Figure 3.3.
Figure 3.2: SEI SEM micrographs of the voided epoxies that have been cryofractured and gold coated. a) EPON 825-AEP w/ 17% hexane by weight (fracture specimen). b) EPON 825-AEP w/ 17% hexane by weight (hollow cylinder). c) EPON 828-AEP w/ 29% propylbenzene by weight (fracture specimen). d) EPON 828-AEP w/ 29% propylbenzene by weight (hollow cylinder).
$T_g = 49.5^\circ C$; 17% propylbenzene

$f = 0.02$; $\overline{D} = 1.7 \pm 0.5\mu m$

$T_g = 49.5^\circ C$; 18% propylbenzene

$f = 0.06$; $\overline{D} = 2.1 \pm 0.3\mu m$

$T_g = 48.3^\circ C$; 19% propylbenzene

$f = 0.08$; $\overline{D} = 2.4 \pm 0.5\mu m$

$T_g = 48.6^\circ C$; 19% propylbenzene

$f = 0.9$; $\overline{D} = 2.4 \pm 0.4\mu m$

$T_g = 53.0^\circ C$; 19% propylbenzene

$f = 0.14$; $\overline{D} = 3.2 \pm 0.8\mu m$

$T_g = 50.4^\circ C$; 20% propylbenzene

$f = 0.22$; $\overline{D} = 4.3 \pm 1.2\mu m$

Figure 3.3: SEI SEM micrographs of the voided epoxy compression bullets that have been cryofractured and gold coated.
Figure 3.3 continued.
3.3 Sample Fabrication

We chose a specimen geometry and test configuration that allows us to continuously vary the state of stress from uniaxial compression to biaxial tension. All multiaxial tests were conducted on thin walled hollow cylinders, shown in Figure 3.4. Fabrication of these specimen requires a two step process. The first step involves spin-casting the hollow tube (Figure 3.5a). A pre-measured amount of epoxy is poured into a stainless steel mold, which is then mounted into a specially designed lathe. While spinning, radiant heat is applied to gel the epoxy. After gelation, the epoxy tube is removed from the mold, the thickness is measured and the ends are corked. In the second step, the end caps are molded onto the hollow cylinder, using a self-aligning mold with a “dumbbell” configuration (Figure 3.5b). Before the final post cure, the hollow cylinder specimen is removed from the mold and a pressure port is tapped. Finally the sample is stored in a desiccator.

All other standard tensile, compression, and fracture toughness specimen are cast in 3.3 mm thick plaques and 11 mm diameter by 22 mm rods. ASTM D638 Type I tensile bars were milled, along with 11 mm by 14 mm bars for Dynamic Mechanical Thermal Analysis (DMTA). All fracture toughness specimen were machined into three point bend specimen of dimensions ¼ x ¾ x 5 inches, using a specially design router and die. The samples were then stored in a desiccator.
Figure 3.4: Thin-walled hollow cylinder specimen geometry.
Figure 3.5: (a) The thin walled hollow cylinders are fabricated using a spin casting process. (b) In a second step, the cylinders are end-capped in a self aligning mold.
3.4 Testing Procedure

Our test strategy focuses on keeping the octahedral shear strain rate, $\dot{\gamma}^{\text{oct}}$, constant for each test, over all stress states. This approach allows us to consistently interrogate the strain rate effects while changing the state of stress.

All standard tensile, compression and fracture toughness tests are conducted in accordance with the ASTM standard. The axial strain rate is controlled by crosshead speed, while both axial and transverse extensometers are attached (most of the time) to the tensile samples to measure strains. The testing temperature is maintained in an environmental chamber, where samples are conditioned for 30 minutes prior to testing.

The hollow cylinders are tested in an Instron 1321 biaxial tension-torsion machine modified with a Tescom ER3000 digitally controlled pressure regulator, Figure 3.6. The grips for this hollow cylinder testing apparatus were specially designed to ensure proper alignment of the sample during testing. Both the top and bottom grips are shown in Figure 3.7. The samples were pressurized with either nitrogen gas or silicon oil, with no measurable difference found in the yield or fracture strength. Note that the difference in clean-up time following sample failure was measurable. Silicon oil was only used with the aliphatic epoxies. For all other samples, nitrogen gas was used. Both the tension-torsion machine and the pressure regulator were externally controlled through a personal computer using a program written in LabVIEW. The hollow cylinders were tested in stress states varying from uniaxial compression to biaxial tension. The LabVIEW test control program maintained a pre-specified state of stress, while monotonically loading the tubes to failure. All tests were conducted at a constant octahedral shear strain rate, $\dot{\gamma}^{\text{oct}}$,.
Figure 3.6: Photograph of the hollow cylinder testing facility. The hollow cylinder specimen is axially loaded in the biaxial testing machine, while internal pressure is supplied from the computer controlled pressure regulator at top of photo.
Figure 3.7: (a) Schematic drawing of the top stainless steel grip in the hollow cylinder testing facility. (b) Schematic drawing of the bottom stainless steel grip in the hollow cylinder testing facility.
Figure 3.7 continued.
for a given failure envelope. Details of this procedure are outlined in the following paragraphs.

The axial and hoop stresses imposed on a thin walled hollow cylinder, subjected to an axial load, \( L \), and internal pressure, \( p \), can be written as:

\[
\sigma_a = \left( \frac{L}{\pi D t} + \frac{pD}{4t} \right) \tag{3.2}
\]

\[
\sigma_h = \left( \frac{pD}{2t} \right) \tag{3.3}
\]

where \( D \) is the mean diameter and \( t \) is the thickness of the tube. In the absence of applied torsion, \( \sigma_a \) and \( \sigma_h \) are the principle stresses. The octahedral shear stress, \( \tau^{\text{oct}} \), and hydrostatic stress, \( \sigma_m \), can be written as follows:

\[
\tau^{\text{oct}} = \frac{1}{3} \sqrt{(\sigma_a - \sigma_h)^2 + (\sigma_h - \sigma_a)^2 + (\sigma_a - \sigma_h)^2} \tag{3.4}
\]

\[
\sigma_m = \frac{1}{3} (\sigma_a + \sigma_h) \tag{3.5}
\]

The corresponding principle strains were calculated using equations (3.6-3.8).

\[
\varepsilon_a = \frac{1}{E} (\sigma_a - \nu \sigma_h) \tag{3.6}
\]

\[
\varepsilon_h = \frac{1}{E} (\sigma_h - \nu \sigma_a) \tag{3.7}
\]

\[
\varepsilon_r = \frac{-\nu}{E} (\sigma_a + \sigma_h) \tag{3.8}
\]

where \( \varepsilon_a \), \( \varepsilon_h \) and \( \varepsilon_r \) are the strains in the axial, hoop and radial directions, \( E \) is the tensile modulus, and \( \nu \) is Poisson’s ratio.
Preliminary tests were conducted on test specimens with extensometers attached to measure $\varepsilon_a$ and $\varepsilon_h$. These tests were used in conjunction with equations (3.6-7) to measure and verify elastic properties. $\varepsilon_r$ was never measured in this study and was calculated using equation (3.8). For the final tests, in which specimens were tested to failure, the extensometers were removed and equations (3.6-8) were used to calculate strains.

Consistent with linear viscoelastic behavior, we chose to keep $\dot{\gamma}^{\text{oct}}$ constant during testing. $\dot{\gamma}^{\text{oct}}$ can be written as:

$$\dot{\gamma}^{\text{oct}} = \frac{1}{3} \sqrt{\left(1 - \frac{\varepsilon_h}{\varepsilon_a}\right)^2 + \left(\frac{\varepsilon_h}{\varepsilon_a} - \frac{\varepsilon_r}{\varepsilon_a}\right)^2 + \left(\frac{1 - \varepsilon_r}{\varepsilon_a}\right)^2 \dot{\varepsilon}_a} \tag{3.9}$$

where $\dot{\varepsilon}_a$ is the axial strain rate. $\dot{\varepsilon}_a$ was both measured using an axial extensometer and calculated from the applied stressing rates as follows:

$$\dot{\varepsilon}_a = \frac{1}{E} \left(\dot{\sigma}_a - v\dot{\sigma}_h\right) \tag{3.10}$$

where $\dot{\sigma}_a$ and $\dot{\sigma}_h$ are the stressing rates in the axial and hoop directions. As in the case of the tensile tests, the axial strain rate was controlled by the crosshead speed. Note that when testing to failure, an axial strain rate is prescribed through the crosshead speed, and $\dot{\gamma}^{\text{oct}}$ is calculated in the elastic region using equations (3.6-10). Therefore $\dot{\gamma}^{\text{oct}}$ is only strictly held constant at the desired rate in the linear elastic regime.
CHAPTER 4

SINGLE-PHASE GLASSY THERMOSETS

4.1 Phenomenological Behavior of Epoxy Resins

4.1.1 Standard Thermal and Mechanical Test Results

The effect of changing $M_c$ and backbone stiffness on the glass transition, $T_g$, has been established and is shown is Figure 4.1. The $T_g$’s were determined using a differential scanning calorimeter(DSC) with a ramp rate of 10°C/min. Figure 4.1 shows that the effect of $M_c$ on $T_g$ follows a Fox\(^8\) type relation, as described in equation (2.2).

\[ T_g = T_g^\infty + \frac{\phi}{M_c} \]  

(2.2)

Our aliphatic amine cured system yields a value of $\phi = 38.8$ K kg/mol and $T_g^\infty = 311$ K, while the aromatic amine cured system yields a value of $\phi = 34.8$ K kg/mol and $T_g^\infty = 358$ K. Note that backbone stiffness affects both $\phi$ and $T_g^\infty$.

Figure 4.2 shows how the tensile modulus, $E$, is effected by temperature and $M_c$. At 21°C and $\dot{\gamma}^{\infty} = 0.028$ min\(^{-1}\), all the aliphatic systems had approximately the same value of $E \approx 2.7$ GPa. Crawford similarly showed that $E$ remains relatively unchanged with $M_c$ in the aromatic systems, at $E = 3.1$ GPa\(^5\). The relation between modulus and temperature is similar to that of most glassy thermosets. The results in Figure 4.2 showing that below $T_g$, $E$ is relatively unaffected by changes in $M_c$, has been reported by others\(^4,5\). Results from dynamic mechanical thermal analysis(DMTA) also support this, Figure 4.3. This is
Figure 4.1: Plot of 1/molecular weight between crosslinks vs. glass transition temperature determined by DSC, for aliphatic amine cured EPON 825 and aromatic amine cured EPON 828. (Reproduced from the work of Crawford and Lesser\textsuperscript{9, 55})
Figure 4.2: Tensile modulus versus temperature, for the aliphatic epoxies (DGEBA cured with EDA and MEDA/DMEDA), at $\dot{\gamma}_{\text{oct}} = 0.028 \text{ min}^{-1}$.
Figure 4.3: Flexural storage modulus of the aliphatic epoxies versus temperature at 1Hz using single cantilever beam DMTA. DGEBA cured with EDA and MEDA/DMEDA.
expected since the glassy modulus is controlled by the local chain packing and chain
stiffness and not by higher length scale parameters, such as $M_c$. Figures 4.2 and 4.3 also
demonstrate that we have successfully changed $M_c$ without significantly altering the chain
stiffness or local packing.

Figure 4.4 shows the tensile strength, from ASTM standard tensile bars versus $\Delta T$,
the difference between the testing temperature, $T$, and $T_g$ at $\dot{\gamma}^{\text{oct}} = .028$ min$^{-1}$.

$$ \Delta T = \left( T - T_g \right) $$ (4.1)

In Figure 4.4, aliphatic amine cured samples with the three highest $M_c$ all yielded
with their yield strengths decreasing with increased temperature. When the yield strengths
of the materials with different $M_c$ are compared at the same temperature shift below $T_g$, i.e.
constant $\Delta T$, they collapse to a single curve. This $\Delta T$ dependence is described by equation
(2.1),

$$ \sigma_y = \sigma_{y}^{T_g} + \alpha \left( T - T_g \right) \text{ for } T<T_g $$ (2.1)

and suggests that with regard to yield strength, the primary effect of changing $M_c$ is a shift
in $T_g$. There is a possible exception with regard to the materials with $M_c=380$ and 480
grams/mol. The samples with $M_c = 480$ grams/mol fail in a brittle fashion in uniaxial
tension at the lower temperatures, but change their mode of failure from brittle fracture to
ductile yield at approximately 40°C. Even at these higher temperatures, the yield strengths
of the material with $M_c=480$ grams/mol do not fully collapse to the curve with the higher
$M_c$ materials. The implications of this will be discussed in section 4.3, and section 4.4 of
Figure 4.4: ASTM D638 tensile strength versus T-T<sub>g</sub>, for aliphatic amine cured EPON 825, at \( \dot{\gamma}^{oc} = 0.028 \text{ min}^{-1} \). Solid and hollow symbols represent yield and fracture. The slope below \( T_g \) is \( \alpha \) and the tensile yield strength extrapolated to \( T_g \) is \( \sigma_y^{T_g} \).
this thesis will explain the reason for the imperfect collapse. As for the samples with $M_c = 380$ grams/mol, brittle fracture is the failure mode regardless of temperature. This a consequence of a network so tightly crosslinked that the yield response is suppressed and brittle fracture is preferred in this stress state.

Again from the ASTM standard tensile bars, if the strain rate is increased, $\sigma_y$ increases in a fashion consistent with a thermally activated process, as illustrated in Figure 4.5. Note that for the aliphatic epoxy with $M_c=950$ grams/mol, $\sigma_y/T$ increases linearly with the logarithm of the strain rate in accordance with an Eyring type equation:

$$\frac{\sigma_y}{T} = \frac{\Delta E}{Tv} + \frac{R}{v} \ln \left( \frac{\dot{\varepsilon}}{\Gamma} \right)$$ \hspace{1cm} (4.2)$$

where $\Delta E$ is the activation energy, $v$ is the activation volume, $\dot{\varepsilon}$ is the strain rate, and $\Gamma$ is a proportionality constant. Figure 4.5 shows that the rate and temperature dependent tensile yield behavior of these materials fits an Eyring type flow model quite well, and is therefore described by equation (2.5). Please note that equation (4.2) should not be used to calculate the activation volumes of yield ($v$ and $\Omega$), because it neglects the effect of hydrostatic stress. For further explanation of this see section 4.4. The activation volume and energy for the aliphatic epoxy with $M_c=950$ grams/mol was found to be $v=3.8$ nm$^3$ and $\Delta E=247$ kJ/mol, using equation (2.5).
Figure 4.5: ASTM D638 tensile yield strength vs. axial strain rate, for aliphatic amine cured EPON 825, $M_c = 950$ grams/mol. The slope of the data set at $21^\circ C$ is $1.57 \times 10^{-2}$ (MPa · min/ K).
4.1.2 Hollow Cylinder Test Results

Quite often, it is useful to compare the stress-strain response when evaluating standard tensile or compressive test results. Similarly, when testing polymeric materials in multiaxial stress states, it is useful to study how volumetric strains affect the mode of failure and the yield or fracture strength of the material. Therefore a plot of the octahedral shear stress, $\tau_{\text{oct}}$, verse engineering volumetric strain, $\varepsilon_v$,

$$\varepsilon_v = (\varepsilon_a + \varepsilon_h + \varepsilon_r) \quad (4.3)$$

provides a qualitative understanding of the loading path under which these tests are run and clearly shows where the ductile-to-brittle transition occurs. Figure 4.6 illustrates this for the case of the aliphatic epoxy with $M_c=380$ grams/mol. Note that from this plot, the ductile-to-brittle transition occurs midway between uniaxial compression and pure shear.

A convenient way to present the yield and brittle response in constrained stress states is to plot the shear yield stress that occurs in the octahedral plane, $\tau_{y\text{oct}}$, as a function of the hydrostatic stress, $\sigma_m$, that occurs in that stress state. If the material follows a modified von Mises type behavior, then the data will plot on a straight line, as described by equation 2.4.

$$\tau_{y\text{oct}} = \tau_{\gamma_0} - \mu\sigma_m \quad (2.4)$$

If $\sigma_m$ has no effect on $\tau_{y\text{oct}}$, as is the case for metals, then the data will plot on a horizontal line and the data is said to follow a typical von Mises behavior. If however $\sigma_m$ does influence $\tau_{y\text{oct}}$, then the line will be sloped. The slope of the line, $\mu$, is commonly referred to as the coefficient of internal friction. This is illustrated in Figure 4.7.
Figure 4.6: Octahedral shear stress vs. engineering volumetric strain on hollow cylinders, illustrating a ductile-to-brittle transition for the aliphatic amine cured EPON 825 with $M_c = 380$ grams/mol.
Figure 4.7: Schematic of the failure envelope of a material that follows a modified von Mises type criterion and has an accessible ductile-to-brittle transition.
Following the above scheme, typical results from our hollow cylinder tests are shown in Figure 4.8. Also in Figure 4.8, we have plotted Sultan and McGarry's results from testing hollow cylinders of a DGEBA (Shell EPON 828) cured with Shell Corporation's curing agent D. Both sets of results show that the yield behavior of epoxy networks follows a modified von Mises criterion. However, McGarry reported a value of $\mu = 0.175$, which differs from our reported value of $\mu = 0.157$ for $M_c = 640$ grams/mol.

Nonetheless, Figure 4.8 shows that McGarry's data agrees quite well with our results. We attribute differences in the reported values of $\mu$ to the scatter introduced in McGarry's data at higher hydrostatic stress levels, which reflects the difficulty of running accurate experiments in this regime.

Figure 4.9 shows the effects that changes in $M_c$ have on the generalized yield and fracture strengths of epoxy materials. In Figure 4.9, ductile yield and brittle fracture are represented by solid and hollow symbols, respectively. Note that the yield behavior follows a modified von Mises criterion for all $M_c$ tested (see equation 2.4). Further, these results show that changing $M_c$ has the effect of changing $\tau^{\text{sci}}_{y_0}$ only, while $\mu$ is independent of $M_c$.

For reference, yield results from uniaxial compression and tensile bars have also been plotted in Figure 4.9. For all $M_c$, the standard tensile and compressive yield strengths are very close to the hollow cylinder results.

Figure 4.9 also shows that as $M_c$ decreases, a ductile-to-brittle transition appears. As shown previously in Figure 4.6, for $M_c = 380$ grams/mol this ductile-to-brittle transition occurs midway between uniaxial compression and pure shear. Although further testing is needed to elucidate the actual brittle failure envelope and the effects that changing $M_c$ has
Figure 4.8: Hollow cylinder octahedral shear yield stress versus hydrostatic stress, for our aliphatic amine cured EPON 825 with $M_c=640$ grams/mol and $\dot{\gamma}_{\text{oct}}=0.028$ min$^{-1}$; and McGarry's results$^{11}$. 
Figure 4.9: Octahedral shear yield stress versus hydrostatic stress, for hollow cylinders made aliphatic amine cured EPON 825 and tested at $\dot{\gamma}^{\text{oct}} = 0.028 \text{ min}^{-1}$. The solid symbols, hollow symbols and ‘+’s represent ductile yield, brittle fracture, and standard compression and tensile yield results, respectively.
on brittle fracture, two statements can be made: First, the fracture strength of these 
materials is more significantly influenced by $\sigma_m$ than is the corresponding yield strength. 
And second, the onset of location of ductile-to-brittle transition is sensitive to changes in $M_c$.

In addition to changing $M_c$, strain rate was also varied. Figure 4.10 shows that for 
aliphatic epoxies with $M_c=950$ grams/mol, tested at $21^\circ C$ and $\dot{\gamma}^{\text{oct}}=0.0028$, $0.028$ and $0.28$ 
min$^{-1}$, only $\tau_{\gamma_0}^{\text{oct}}$ is affected by a change in strain rate. $\mu$ remains insensitive to changes in 
$\dot{\gamma}^{\text{oct}}$, with $\mu = 0.172, 0.163, \text{and 0.173 for } \dot{\gamma}^{\text{oct}}=0.0028, 0.028 \text{ and 0.28 min}^{-1}, \text{respectively.}$ 
This is in contrast to the general statement made by Kinloch$^{24}$, regarding the effects of 
strain rate on $\mu$ (see Section 2.1.2). However tests by Duckett et. al. have also shown $\mu$ to 
be insensitive to strain rate$^{13}$. Further consideration of the manner in which $\mu$ is affected by 
testing conditions is given in Section 4.4. Furthermore, the $\dot{\gamma}^{\text{oct}}$ induced increase in $\tau_{\gamma_0}^{\text{oct}}$ 
can be directly compared with our tensile data for the same material (see Figure 4.5). The 
hollow cylinders showed a strain rate dependence on $\tau_{\gamma_0}^{\text{oct}}$ of $2.6$ MPa per decade increase in 
strain rate, which is close to the $2.2$ MPa per decade obtained for the tensile tests at $21^\circ C$. 
Note the strain rate dependence on yield should be lower for uniaxial tension than for pure 
shear, as is described in Section 4.4.2.

In Section 4.4, we further describe the effects of temperature, strain rate and 
backbone structure on $\tau_{\gamma_0}^{\text{oct}}$ and $\mu$. This work was completed by testing tensile bars, 
compression bullets and hollow cylinders made of both aliphatic and aromatic amine cured 
epoxy, while varying $M_c$, temperature and strain rate.
Figure 4.10: Octahedral shear yield stress versus hydrostatic stress, for hollow cylinders made of aliphatic amine cured EPON 825 with $M_c=950$ grams/mol, tested at varying strain rates.
4.2 Formulation of a Generalized Yield Model for Glassy Polymer Networks

To develop a generalized model to describe the yield behavior of single-phase glassy polymers networks, we start by considering the assumptions detailed by Robertson\textsuperscript{25} and Ward\textsuperscript{12} in deriving equation (2.5).

\[ \dot{\gamma} = \Gamma \exp \left( - \frac{\Delta E - \tau_y \nu + p\Omega}{RT} \right) \]  

(2.5)

We then apply equation (2.5) to the octahedral shear stress, \( \tau_y^{\text{oct}} \), and octahedral shear strain rate, \( \dot{\gamma}^{\text{oct}} \). Taking \( \sigma_m \) as positive to denote hydrostatic tension, equation (2.5) takes the form:

\[ \dot{\gamma}^{\text{oct}} = \Gamma \exp \left( - \frac{\Delta E - \tau_y^{\text{oct}} \nu - \sigma_m \Omega}{RT} \right) \]  

(4.4)

It can be shown that equation (4.4) can be expressed in the form of equation (2.4)

\[ \tau_y^{\text{oct}} = \tau_y^{\nu_0} - \mu \sigma_m \]  

(2.4)

with:

\[ \tau_y^{\nu_0} = \frac{\Delta E}{\nu} + \frac{RT}{\nu} \ln \left( \frac{\dot{\gamma}^{\text{oct}}}{\Gamma} \right) \]  

(4.5)

\[ \mu = \frac{\Omega}{\nu} \]  

(4.6)

Notice that equations (4.5) and (4.6) show that only \( \tau_y^{\nu_0} \) is affected by changes in \( \dot{\gamma}^{\text{oct}} \) and \( T \). In equation (4.6), \( \mu \) describes the ratio of the activation volumes for dilation and shear of the polymer and is independent of \( T \) and \( \dot{\gamma}^{\text{oct}} \). Consequently, this model agrees with the phenomenological observations described in Section 4.1. with regard to strain rate and test
temperature (see Figures 4.4, 4.5 and 4.10). However these tests do not provide evidence as to whether or not \( \mu \) is affected by temperature.

Recall that the yield response of the epoxies was empirically described by equation (2.1).

\[
\sigma_y = \sigma_y^{T_g} + \alpha \left( T - T_g \right) \quad \text{for } T < T_g
\]  

(2.1)

This demonstrates that \( \sigma_y \) can be approximated by the yield strength at a reference temperature, \( \sigma_y^{T_g} \), with a linear increase in \( \sigma_y \) as the testing temperature is decreased below \( T_g \). Again equation (2.1) is valid only while stress state and strain rate remain unchanged.

Note that equation (4.5) has the same linear dependence with regard to temperature as equation (2.1). From this linear temperature dependence, along with the strain rate dependence of equation (4.5), one can express equation (4.5) in the form of equation (2.1) as follows:

\[
\tau_\gamma^{\text{oct}} = \tau_\gamma^{\text{oct}} \frac{\text{RT}_g}{v} \ln \left( \frac{\dot{\gamma}^{\text{oct}}}{\dot{\gamma}_r^{\text{oct}}} \right) + \left( T - T_g \right) \frac{R}{v} \ln \left( \frac{\dot{\gamma}^{\text{oct}}}{\Gamma} \right)
\]  

(4.7)

where \( \tau_\gamma^{\text{oct}} \) represents \( \tau_\gamma^{\text{oct}} \) at \( T_g \) and some reference strain rate, \( \dot{\gamma}_r^{\text{oct}} \). The second term on the right hand side of equation (4.7), \( \frac{\text{RT}_g}{v} \ln \left( \frac{\dot{\gamma}^{\text{oct}}}{\dot{\gamma}_r^{\text{oct}}} \right) \), reflects the offset in \( \tau_\gamma^{\text{oct}} \) at \( T_g \) that results when testing at some strain rate, \( \dot{\gamma}^{\text{oct}} \), which differs from \( \dot{\gamma}_r^{\text{oct}} \). The last term, \( \left( T - T_g \right) \frac{R}{v} \ln \left( \frac{\dot{\gamma}^{\text{oct}}}{\Gamma} \right) \), contains the linear dependence of \( \tau_\gamma^{\text{oct}} \) on \( T \) at the testing strain rate,
Substituting equations (4.6) and (4.7) into equation (2.4), one obtains an expression for the yield of a glassy polymer in a generalized state of stress:

$$\tau_0^{\text{oct}} = \tau_0^{\text{oct}} + \frac{RT}{\nu} \ln \left( \frac{\dot{\gamma}_r^{\text{oct}}}{\dot{\gamma}_r} \right) + \left( T - T_e \right) \frac{R}{\nu} \ln \left( \frac{\dot{\gamma}_r^{\text{oct}}}{\Gamma} \right) - \mu \sigma_m$$

Consequently, equation (4.8) provides a general expression for predicting $\tau_0^{\text{oct}}$ for any given $T$, $\dot{\gamma}$, and state of stress. The effect of temperature, stress state and strain rate on $\tau_0^{\text{oct}}$ is illustrated in Figure 4.11.

Finally, equation (4.8) can be extended to include the Fox expression for $T_g$ (equation 2.2) for crosslinked systems.

$$T_g = T_g^{\infty} + \frac{\phi}{M_c}$$

For crosslinked resins, equation (4.8) takes the following form:

$$\tau_0^{\text{oct}} = \tau_0^{\text{oct}} + \left( T_g^{\infty} + \frac{\phi}{M_c} \right) \frac{R}{\nu} \ln \left( \frac{\dot{\gamma}_r^{\text{oct}}}{\dot{\gamma}_r} \right) + \left( T - T_g^{\infty} + \frac{\phi}{M_c} \right) \frac{R}{\nu} \ln \left( \frac{\dot{\gamma}_r^{\text{oct}}}{\Gamma} \right) - \mu \sigma_m$$

Equation (4.9) allows for predicting how $\tau_0^{\text{oct}}$ will change, as $M_c$, $\phi$ and $T_g^{\infty}$ of a crosslinked thermoset is altered, in addition to the $T$, $\dot{\gamma}$, and stress state effects. Moreover, this model is a “working model” in the sense that the parameters used in it can be readily determined from standard mechanical and thermal tests and modified as we learn more about each of the parameters in the model.
Figure 4.11: Schematic illustrating the manner in which testing temperature, strain rate, and state of stress affect the yield strength, as described by equation (4.8).
4.3 Comparison of Model with Experimental Results

Using results from ASTM standard tensile tests and thermal tests, shown in Figures 4.4, 4.7 and 4.8, and inserting them into equation (4.9), \( \tau_{y}^{\text{oct}} \) can be determined for any given \( M_c, \phi, T_g, \gamma, \gamma^*, \) and stress state. \( \tau_{y0(\gamma, T)}^{\text{oct}} \) was calculated from the results in Figure 4.4a, using the offset level in the tensile yield strength at \( T_g, \sigma_{y0}^{\text{T}} \), with \( \gamma_r^{\text{oct}} = 0.028 \text{ min}^{-1} \) and the relationship:

\[
\tau_{y0(\gamma, T)}^{\text{oct}} = \frac{\sqrt{2}}{3} \sigma_{y0}^{\text{T}} + \frac{1}{3} \mu \sigma_{y0}^{\text{T}}
\]  

(4.10)

The ratio \( R/v \) in equation (4.9) is calculated from the tensile data presented in Figure 4.5 along with the relationship:

\[
\frac{R}{v} = \frac{\tau_{y2}^{\text{oct}} - \tau_{y1}^{\text{oct}}}{T \ln \left( \frac{\gamma_2^{\text{oct}}}{\gamma_1^{\text{oct}}} \right)}
\]  

(4.11)

where \( \tau_{y1}^{\text{oct}} \) and \( \tau_{y2}^{\text{oct}} \) are the octahedral shear yield stresses measured at two different octahedral strain rates, \( \gamma_1^{\text{oct}} \) and \( \gamma_2^{\text{oct}} \), respectively. Values for \( T_g^{\circ} \) and \( \phi \) were obtained from the DSC data in Figure 4.1. \( \Gamma \) is calculated as follows:

\[
\Gamma = \frac{\gamma_1^{\text{oct}}}{\exp \left( \frac{\gamma_1^{\text{oct}}}{\gamma_1^{\text{oct}}} \right)}
\]  

(4.12)

where \( \alpha \) is calculated from Figure 4.4 using equation (2.1), and corrected to account for the octahedral shear stress. Finally, \( \mu \) can be determined from hollow cylinder tests (e.g., Figures 4.9 and 4.10) or by conducting uniaxial tension and compression tests on the resin.
For these comparisons a value of \( \mu = 0.166 \) was used for the aliphatic epoxies. This is the average value obtained from the hollow cylinder tests, over all \( M_c \) and \( \dot{\gamma}^{\text{oc}} \) tested. Note that of all the parameters input into the model for predicting the hollow cylinder results, \( \mu \) is the only parameter that has come from the hollow cylinder test results.

Figure 4.12 presents the comparisons between hollow cylinder experimental data and the model predictions using equation (4.9) for three different strain rates. The model predictions are plotted as solid lines, and the yield data as solid symbols. For the aliphatic case of \( M_c = 950 \) grams/mol, equation (4.9) predicts the yield strength quite well over stress states ranging from uniaxial compression to biaxial tension, and over three orders of magnitude of strain rates. The accuracy with which equation (4.9) predicts the yield response is even more impressive, given the fact that the rate dependence on yield strength that was used in the model came from the ASTM standard tensile data.

Similarly, Figure 4.13 presents a comparison plot for five different \( M_c \) resin systems. Again, the hollow cylinder yield data in Figure 4.13 are plotted with solid symbols, the brittle failures are plotted with hollow symbols and the model predictions are presented by the solid lines. Careful evaluation of Figure 4.13 indicates that equation (4.9) describes the yield response of the DGEBA cured with the EDA and MEDA/DMEDA over the higher values of \( M_c \). At the low \( M_c \) values of 380 and 480 grams/mol, equation (4.9) over estimates the yield response of these materials by as much as 10%. This is consistent with the response observed in Figure 4.4a, where the tensile yield strength of the \( M_c = 380 \) and \( M_c = 480 \) grams/mol did not collapse with the yield data of the higher \( M_c \) materials.
Figure 4.12: Octahedral shear yield stress versus hydrostatic stress, for hollow cylinders made aliphatic amine cured EPON 825 with $M_c=950$ grams/mol, tested at varying octahedral shear strain rates. The solid symbols represent ductile yield and the lines represent the yield response predicted from equation (4.9).
Figure 4.13: Octahedral shear yield stress versus hydrostatic stress, for hollow cylinders made aliphatic amine cured EPON 825 and tested at $\dot{\gamma}_{oct} = .028$ min$^{-1}$. The solid symbols, hollow symbols, and lines represent ductile yield, brittle fracture, and predicted yield response from equation (4.9), respectively.
Further studies, described in the section 4.4 and 4.5, have identified and resolved the causes of the discrepancy.

Note that the application of equation (4.9) implies that all of the epoxy networks tested have the same activation volumes for shear, \( v \), and dilation, \( \Omega \). That is, the introduction of crosslinks into these polymers does not change the activation volumes necessary for yielding. Also Note that equation (4.9) implies that changing \( T_g \) is the same as changing \( T \). Also the model predicts that the activation energies, \( \Delta E \) of the epoxies increase with the introduction of crosslinks and are directly related to the \( T_g \) of the resins. Since the model does not predict the yield behavior of epoxies with low values of \( M_c \), one of these two assumptions may be incorrect.

As previously stated, we have further tested the effects of changing temperature, strain rate, stress state, \( M_c \) and backbone stiffness on the yield behavior of glassy networks. These studies have allowed us to further evaluate equation (4.9) and make modifications to the model as appropriate.

4.4 Further Evaluation of the Phenomenological Yield Behavior of Epoxy Resins

In this section, we report results that more thoroughly consider the effects of changing stress state, strain rate, temperature, \( M_c \) and backbone stiffness on the yield behavior of glassy epoxy networks. These studies have allowed us to further evaluate their yield behavior and make modifications to equation (4.9) as appropriate.
Before we more thoroughly describe the phenomenological yield of the epoxy resins, in the next two paragraphs we will review the reasons for extending this work and the shortcomings of the previously proposed yield model (equation 4.9). We start by recalling that equation (4.9) was developed to predict how \( \tau_{\gamma}^{\text{oct}} \) will change, as \( M_c \), \( \phi \) and \( T_{go} \) of a crosslinked thermoset are altered, in addition to the \( T \), \( \dot{\gamma}^{\text{oct}} \), and stress state effects.

The ability of this model to collapse the yield response on aliphatic epoxies of varying \( M_c \) that were tested over a range of stress states and strain rates is shown in Figure 4.14. Please note that Figure 4.14 contains the same information as Figure 4.12 and 4.13, only in a collapsed manner. Careful evaluation of Figure 4.14 indicates that equation (4.9) accurately describes the yield response of the aliphatic epoxy system over stress states ranging from uniaxial compression to biaxial tension and over two orders of magnitude change in strain rate. However with regard to the effect of changing \( M_c \), equation (4.9) can overestimate the yield response of the lowest \( M_c \) materials by as much as 10%.

The application of equation (4.9) implies that the activation volumes for shear, \( \nu \), and dilation, \( \Omega \), and hence the value for \( \mu \) remain unchanged as \( M_c \) of the epoxy networks and the testing temperature are changed. That is, the introduction of crosslinks into these polymers does not change the activation volumes necessary for yielding. Also equation (4.9) implies that changing \( T_g \) has the same effect on yield as changing \( T \). This also implies that the activation energy for yield in a glassy network, \( \Delta E \) described in equation (2.5), should be directly related to the \( T_g \) of the resin. Since equation (4.9) does not predict the yield behavior of epoxies with low values of \( M_c \), one or more of these assumptions may be
incorrect. And this is the reason that we must more thoroughly investigate the yield behavior of the single-phase epoxy networks.
Figure 4.14: Octahedral shear yield stress versus hydrostatic stress, for hollow cylinders made aliphatic amine cured EPON 825 with varying $M_c$ and tested at $\gamma^{\text{oct}} = 0.0028, 0.028, 0.28$ min$^{-1}$. The solid symbols represent ductile yield strengths of the hollow cylinders, all collapsed to the yield response of the aliphatic epoxy with $M_c=950$ grams/mol and tested at $\gamma^{\text{oct}} = 0.028$ min$^{-1}$, as predicted by equation (4.9).
4.4.1 Effect of Temperature and $T_g$ on Yield Strength

In the phenomenological development of equation (4.9), it was reported in Section 2.1.1 that the tensile yield strength, $\sigma_y$, of aliphatic epoxy networks tested below $T_g$, could be approximated by the following empirical expression\textsuperscript{7,56}:

$$\sigma_y = \sigma_{y}^{T_g} + \alpha(T - T_g) \text{ for } T < T_g \quad (2.1)$$

where $\sigma_{y}^{T_g}$ represents the yield stress at $T_g$, and $\alpha$ is a negative term that describes the linear increase in $\sigma_y$ as $T$ is decreased below $T_g$. However this equation described our previous tensile results (Figure 4.4), which only covered a narrow range of temperatures, because the materials failed by a brittle mode at the lower temperatures.

To more thoroughly study the effect of $T$ and $T_g$ on yield, both aromatic and aliphatic systems were tested in uniaxial compression over a much broader range of temperatures, see Figures 4.15 and 4.16. From Figures 4.15 and 4.16, we see that over a wider range of temperatures, the yield strengths of epoxy networks do not collapse according to equation (2.1). Figure 4.17 provides a better understanding of the effect of both $T$ and $T_g$ on the yield strength of epoxies. Figure 4.17 shows that the yield strength of an aromatic epoxy with $M_c=900 \text{ grams/mol}$ increases with a change in $T$ (by a slope $\alpha$) and the yield strength of aromatic epoxies increase with an increase in $T_g$ (by a slope $\delta$). From this plot we see that changing $T$ has a greater effect on the yield strength than changing $T_g$ does, and hence the ratio, $\beta = \frac{\alpha}{\delta}$, is always less than 1. This makes sense, as changing $T_g$ through a change in $M_c$ has been shown to have no effect on the backbone stiffness or packing density(intermolecular interactions) and primarily affects the intramolecular energy.
Figure 4.15: Compressive strength versus T-T_g, for (aromatic epoxies) EPON 828 cured with MPDA and Aniline, at \( \dot{\gamma} \text{oct} = 0.028 \text{ min}^{-1} \).
Figure 4.16: Compressive strength versus $T-T_g$, for (aliphatic epoxies) EPON 825 cured with EDA and MEDA/DMEDA, at $\dot{\gamma}_{oct} = 0.028$ min$^{-1}$.
Figure 4.17: Compressive yield strength versus $T-T_g$. (A) for aromatic epoxies with varying $M_c$ (varying $T_g$) that were tested at 21°C, and (B) an aromatic epoxy with $M_c = 900$ grams/mol that was tested at varying temperatures.
barrier. Meanwhile, changing T would more significantly affect the intermolecular energy barriers. Note in Figures 4.17, that α and therefore β may both change as the temperature is changed through the secondary relaxations. We will discuss this further in Section 4.4.2. A similar conclusion can be derived for the aliphatic epoxies.

Figures 4.18 and 4.19 show that below $T_g$, the yield strength, $\sigma_y$, of both the aromatic and aliphatic resins can more accurately be phenomenologically approximated by the following expression:

$$\sigma_y = \sigma_y^T + \alpha(T - \beta T_g) \text{ for } T < T_g$$  \hspace{1cm} (4.13)

where $\sigma_y^T$ represents the yield stress at some temperature $T = \beta T_g$,

$\alpha$ describes the linear increase in $\sigma_y$ as $T$ is decreased below $T_g$ (see Figure 4.17),

$\beta$ describes the ratio of the effect of changing $T_g$ to that of changing $T$ on the yield strength of the network, $\beta = \delta / \alpha$,

and hence the product $\alpha \beta = \delta$ describes the linear increase in $\sigma_y$ as $T_g$ is increased.

Under a state of uniaxial compression, for the aromatic system: $\alpha = 0.83$ MPa/K and $\beta = 0.30$ and for the aliphatic system: $\alpha = 0.98$ MPa/K and $\beta = 0.61$. Again equation (4.13) is only valid if the stress state and strain rate are unchanged.
Figure 4.18: Compressive yield strength versus $T - \beta T_g$, where $\beta$ describes how much less the yield strength is affected by a change in $T_g$ than it is affected by a change in $T$. The results are for aromatic amine cured epoxies (EPON 828 cured with MPDA and aniline), tested at $\dot{\gamma}^{\text{oct}} = 0.028 \text{ min}^{-1}$. 

\[
\sigma_y^{\text{c}}(T) = 261.3 \\
\alpha = 0.8279875 \\
\delta = 0.2482445 \\
\beta = 0.2998 
\]
Figure 4.19: Compressive yield strength versus $T-\beta T_g$, where $\beta$ describes how much less the yield strength is affected by a change in $T_g$ than it is affected by a change in $T$. The results are for aliphatic amine cured epoxies (EPON 825 cured with EDA and MEDA/DMEDA), tested at $\dot{\gamma}^{\text{out}} = 0.028 \text{ min}^{-1}$. 

\[
\sigma_y^c (T-\beta T_g) = 154.5
\]

$\alpha = 0.9833$

$\delta = 0.601218$

$\beta = 0.61142886$
4.4.2 Effect of Strain Rate, Temperature and $T_g$ on the $v$, $\Omega$ and $\mu$

As previously shown, equation (4.9) has been shown to accurately predict the effect of strain rate, temperature and stress state on the yield behavior of glassy polymers. However the manner in which the activation volumes for shear, $v$, and dilatation, $\Omega$, and the coefficient of internal friction, $\mu$, are affected by strain rate, stress state, temperature and backbone stiffness is not well understood. For example, it is well known that the strain rate dependence on yield for glassy polymers is greater for uniaxial compression than tension. In the past this has been mistakenly been used to suggest that $\mu$ changes with both strain rate and stress state. We as well as others have already remedied the first of the misinterpretations, by showing $\mu$ to be independent of strain rate, see Figure 4.10. In the following sections, we will more thoroughly show how $v$, $\Omega$ and $\mu$ are affected by stress state, strain rate, temperature and molecular architecture.

4.4.2.1 Effect of Strain Rate and Stress State on Activation Volumes (Theoretical)

To understated why the strain rate dependence on yield is greater for uniaxial compression than uniaxial tension, while $v$, $\Omega$ and $\mu$ all remain independent of stress state, one should consider equation (4.4) for both uniaxial compression and tension.

$$\dot{\gamma}^{oct} = \Gamma \exp \left( - \frac{\Delta E - \tau_y^{oct} v - \sigma_m \Omega}{RT} \right)$$  \hspace{1cm} (4.4)

Please note that equation (4.4) is the base equation, from which our yield model, equation (4.9), was developed. Also note that equation (4.4) can be written in the following form:
\[
\tau_y^{\text{oct}} = \frac{\Delta E}{v} + \frac{RT}{v} \ln \left( \frac{\dot{\gamma}^{\text{oct}}}{\Gamma} \right) - \frac{\Omega}{v} \sigma_m
\]  
(4.14)

For the case of uniaxial compression, the compressive yield strength, \(\sigma_{yc}\), can be substituted into equation (4.14) using the following relations:

\[
\tau_y^{\text{oct}} = \frac{\sqrt{2}}{3} \sigma_{yc} \quad \text{and} \quad \sigma_m = -\frac{\sigma_{yc}}{3}
\]  
(4.15)

resulting in a thermally activated yield model for uniaxial compression:

\[
\frac{\sigma_{yc}}{T} = \frac{3}{(\sqrt{2} - \mu)} \left[ \frac{\Delta E}{vT} + \frac{R}{v} \ln \left( \frac{\dot{\gamma}^{\text{oct}}}{\Gamma} \right) \right]
\]  
(4.16)

where \(\dot{\gamma}^{\text{oct}} = \frac{\sqrt{2}}{3} \dot{\varepsilon}_a\) and \(\dot{\varepsilon}_a\) is the axial strain rate. For the case of uniaxial tension, the tensile yield strength, \(\sigma_{yt}\), can be substituted into equation (4.14) using the following relations:

\[
\tau_y^{\text{oct}} = \frac{\sqrt{2}}{3} \sigma_{yt} \quad \text{and} \quad \sigma_m = \frac{\sigma_{yt}}{3}
\]  
(4.17)

resulting in a thermally activated yield model for uniaxial tension:

\[
\frac{\sigma_{yt}}{T} = \frac{3}{(\sqrt{2} + \mu)} \left[ \frac{\Delta E}{vT} + \frac{R}{v} \ln \left( \frac{\dot{\gamma}^{\text{oct}}}{\Gamma} \right) \right]
\]  
(4.18)

From equations (4.16) and (4.18), one can see why there is a greater strain rate dependence on yield in uniaxial compression than uniaxial tension, for all materials in which \(\mu > 0\).

To further illustrate the point, we will now generate some plots describing the effect of strain rate on the yield stress, for an arbitrary material with \(\mu = 0.2\). For this exercise, we
will use the made-up pure shear stress versus strain rate relations shown in Table 4.1, where
\( \tau_{y0}^{\text{oct}} \) is the octahedral shear yield strength in a state of pure shear.

Table 4.1: Arbitrary pure shear yield strengths for a made up material tested over a range of shear strain rates. The values for \( \dot{\gamma}^{\text{oct}} \) and \( \tau_{y0}^{\text{oct}} \) have been arbitrarily made up. The values for \( \tau_{y}^{\text{oct}} \), in compression and tension, have been calculated using equations (4.16) and (4.18), assuming \( \mu=0.2 \). This data is used to generate Figures 4.20 and 4.21.

<table>
<thead>
<tr>
<th>( \dot{\gamma}^{\text{oct}} ) (mm/mm/min)</th>
<th>( \tau_{y0}^{\text{oct}} ) (MPa)</th>
<th>( \tau_{y}^{\text{oct}} ) (MPa) compression</th>
<th>( \tau_{y}^{\text{oct}} ) (MPa) tension</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.00e-3</td>
<td>1.000</td>
<td>1.165</td>
<td>0.876</td>
</tr>
<tr>
<td>0.01</td>
<td>2.000</td>
<td>2.329</td>
<td>1.752</td>
</tr>
<tr>
<td>0.10</td>
<td>3.000</td>
<td>3.494</td>
<td>2.628</td>
</tr>
<tr>
<td>1.00</td>
<td>4.000</td>
<td>4.659</td>
<td>3.504</td>
</tr>
<tr>
<td>10.00</td>
<td>5.000</td>
<td>5.824</td>
<td>4.381</td>
</tr>
<tr>
<td>100.00</td>
<td>6.000</td>
<td>6.988</td>
<td>5.257</td>
</tr>
<tr>
<td>1000.00</td>
<td>7.000</td>
<td>8.153</td>
<td>6.133</td>
</tr>
</tbody>
</table>

The octahedral shear yield strength of this material in any arbitrary state of stress, \( \tau_{y}^{\text{oct}} \), can be calculated through the modified von Mises equation:

\[
\tau_{y}^{\text{oct}} = \tau_{y0}^{\text{oct}} - \mu \sigma_m
\]  

(2.4)

where in uniaxial compression:

\[
\sigma_m = -\frac{\tau_{y0}^{\text{oct}}}{\sqrt{2}}
\]  

(4.19)

and in uniaxial tension:

\[
\sigma_m = \frac{\tau_{y0}^{\text{oct}}}{\sqrt{2}}
\]  

(4.20)
Substituting the value for $\tau_{y0}^{\text{ref}}$ from Table 4.1 and $\mu = 0.2$ into equations (2.4, 4.19 and 4.20), one can calculate the effect of strain rate on yield strength in both uniaxial compression and tension. The results of this calculation are shown in Table 4.1.

Figure 4.20 shows how the yield stress of this arbitrary material is affected by both strain rate and stress state. Specifically, Figure 4.20 proves that with constant $v$, $\Omega$ and $\mu$, there is a greater strain rate dependence on yield in uniaxial compression than in uniaxial tension.

Moreover for the arbitrary material of Table 4.1, Figure 4.21 plots $\tau_{y}^{\text{ref}}$ versus $\sigma_{m}$, showing how $\tau_{y}^{\text{ref}}$ increases with strain rate more in uniaxial compression than uniaxial tension, while $\mu$ remains constant with changing stress state. With this confirmation, that $v$, $\Omega$, and $\mu$ are unaffected by changing strain rate and stress state, we now turn our attention to understanding how $v$, $\Omega$ and $\mu$ are affected by changes in temperature and $M_c$. 
Figure 4.20: Octahedral shear yield stress versus strain rate (octahedral or axial), for an arbitrary material with $\mu=0.2$ and a yield stress versus strain rate response as described in Table 4.1. The yield response in uniaxial compression and tension is calculated from equations (2.4, 4.19, and 4.20).
Figure 4.21: Octahedral shear yield stress versus hydrostatic stress, for an arbitrary material with $\mu=0.2$ and a yield stress versus strain rate response as described in Table 4.1. The yield response in uniaxial compression and tension is calculated from equations (2.4, 4.19, and 4.20).
4.4.2.2 Effect of Temperature on Activation Volumes and $\mu$

Now we will look at some real experimental results. Evidence of a change in the activation volume and/or volumes at the onset of the $\beta$ transition, can be seen by replotting the data in Figures 4.15 and 4.16 (see Figures 4.22 and 4.23). In Figure 4.22, the compressive yield strength of the aromatic epoxies is plotted versus temperature, showing a change in slope at approximately 20°C. Rewriting equation 4.16 in an alternative form,

$$\sigma_{yc} = \frac{3}{(\sqrt{2} - \mu)} \left[ \frac{\Delta E}{\nu} + \frac{RT}{\nu} \ln \left( \frac{\gamma^{opt}}{\Gamma} \right) \right]$$

(4.21)

shows that a change in the relationship between $\sigma_{yc}$ and temperature, suggests that $\nu$ and/or $\mu$ must have changed. There is also a possibility that $\Delta E$ is changing as well. The change in the slope of the $\sigma_{yc}$ versus temperature plot for the aliphatic epoxy (Figure 4.23) is not as pronounce as for the aromatic epoxy. Two possible reasons for this are that for the aliphatic epoxies: the upper tail of the $\beta$ increases in temperature as $M_c$ decreases, and the Tg’s of the aliphatic epoxies are so low that the $\alpha$ and $\beta$ transitions tend to overlap. Additional work was done to better understand how the activation volumes are affected by temperature.

Figures 4.24 and 4.25 show how the compressive, $\sigma_{yc}$, and tensile, $\sigma_{yt}$, yield strengths of the aromatic epoxy with $M_c=900$g/mol are affected by both strain rate and temperature. From equations (4.16) and (4.18), we see that the slope of the plots in Figures 4.24 and 4.25 are inversely proportional to $\nu$. And in Figure 4.24, note that the slope of the $\sigma_{yc} / T$ versus log of strain rate increases as the temperature is decreased below 20°C.
Figure 4.22: Compressive strength versus temperature, for (aromatic epoxies) EPON 828 cured with MPDA and Aniline, at $\dot{\gamma}^{\text{oct}} = 0.028$ min$^{-1}$. 
Figure 4.23: Compressive strength versus temperature, for (aliphatic epoxies) EPON 825 cured with EDA and MEDA/DMEDA, at $\dot{\gamma}^{\text{ref}} = 0.028 \text{ min}^{-1}$.
Figure 4.24: Compressive yield strength/temperature versus axial strain rate, for the aromatic epoxy with $M_c = 900$ grams/mol and tested over a range of temperatures.
Figure 4.25: ASTM D638 tensile yield strength/temperature versus axial strain rate, for the aromatic epoxy with $M_c = 900$ grams/mol and tested over a range of temperatures.
In light of this increased slope below 20°C, careful examination of equation (4.16),

\[ \frac{\sigma_{yx}}{T} = \frac{3}{(\sqrt{2} - \mu)} \left[ \frac{\Delta E}{vT} + \frac{R}{v} \ln \left( \frac{v^\text{oct}}{\Gamma} \right) \right] \]  

(4.16)
suggests that \( v \) decreases and/or \( \mu \) increases as the temperature is decreased below 20°C. It is important to note that for the aromatic epoxies, the \( \beta \) transition’s upper limit tails off at approximately 20°C (see Figure 4.26). It is therefore believed that \( v \) and/or \( \mu \) change as a material is heated or cooled through this secondary transition.

The exact manner in which \( v \) and/or \( \mu \) change below 20°C is not known, because in uniaxial tension this aromatic epoxy fails in a brittle manner below 20°C. Therefore when we plugged the data from Figures 4.24 and 4.25 into equations (4.16) and (4.18), the effect of temperature on \( v \), \( \Omega \), and \( \mu \) could only be calculated for temperatures of 21°C and higher. Using the compression and tensile results of Figures 4.24 and 4.25, Figures 4.27 and 4.28 show how \( v \) and \( \mu \) are affected by changes in temperature. Figure 4.27 shows that the activation volume for shear, \( v \), appears to remain constant in the temperature range from 21-80°C. However, the compressive data in Figure 4.24 suggest that \( v \) decreases and/or \( \mu \) increases below 20°C. From Figure 4.28, few statements can be made in regard to the effect of temperature on \( \mu \), primarily because of the large scatter in the data. However, since \( \mu \) is related to \( v \) in the following manner, \( \mu = \frac{\Omega}{v} \), it is a reasonable assumption that \( \mu \) is also changed as the temperature is decreased below 20°C (the onset of the \( \beta \) transition).

What is not known is whether this change in \( v \) and/or \( \mu \) is a continuous change with decreasing temperature, or if it is a step to a new value for \( v \) and/or \( \mu \) that remains constant.
Figure 4.26: Log (tan δ) as a function temperature for the aromatic epoxies with varying Mc. This plot has been reproduced from the work of Emmett Crawford and Alan J. Lesser\textsuperscript{55}. 

\[ \log (\tan \delta) \text{ as a function of temperature for the aromatic epoxies with varying } M_c. \]
Figure 4.27: Shear flow activation volume, $v$, versus temperature, for the aromatic epoxy with $M_c = 900$ grams/mol. $v$ was calculated from the compressive and tensile yield response in Figures 4.22 and 4.23, using equations (4.16) and (4.18).
Figure 4.28: Coefficient of internal friction, $\mu$, versus temperature, for the aromatic epoxy with $M_c = 900$ grams/mol. $\mu$ was calculated from the compressive and tensile yield response in Figures 4.22 and 4.23, using equations (4.16) and (4.18).
until the temperature is decreased below another secondary transition. I do understand that the above argument is a bit confusing. Unfortunately, the manner in which the activation volumes change with temperature will remain confusing, until further studies are done to determine the relationship between the activation volumes and temperature.

4.4.2.3 Effect of Temperature and $M_c$ on Activation Volumes

(Hollow Cylinder Approach)

Since the aromatic epoxies are brittle below 20°C in uniaxial tension, the activation volumes and $\mu$ cannot be measured from stand compression and tensile tests. However, $\mu$ can also be measured from hollow cylinder tests. Then by using the compression results in Figure 4.24 and the $\mu$ calculated hollow cylinder tests, equation (4.16) can be used to calculated both $\nu$ and $\Omega$ as a function of temperature and $M_c$. Figure 4.29 shows the yield and brittle strengths of hollow cylinders of aromatic epoxies with $M_c=900$ grams/mol that were tested in stress states ranging from uniaxial compression to biaxial tension. From the slopes of the $\tau_{\text{y}}^{\text{oct}}$ versus $\sigma_m$ plots, $\mu$ is obtained and has been plotted for the aromatic epoxy in Figure 4.30. Both Figures 4.29 and 4.30 show that there is a significant decrease in $\mu$ between the temperatures of 20°C and 50°C. This combined with the change in slope of the $\sigma_{\text{y}} / T$ versus log of strain rate data in Figure 4.24, suggests that when the materials is cooled below the onset of the $\beta$ transition that $\nu$ decreases and $\mu$ increases. These results agree with the work of Bauwens-Crowet, Bauwens and Homes\textsuperscript{22}, who measured the compressive and tensile yield strengths polycarbonate over a range of temperatures. From
there results, we calculated $\mu$ for polycarbonate over a range of temperatures. The results of these calculations as well as the work of others\textsuperscript{10, 54} have been plotted in Figure 4.31.
Figure 4.29: Octahedral shear yield stress versus hydrostatic stress, for hollow cylinders made of aromatic epoxy with $M_c=900$ grams/mol, tested at $\dot{\gamma}_\text{oct} = .028 \text{ min}^{-1}$ and varying temperatures. The solid and hollow symbols represent the yield and brittle strength respectively, and the solid lines represent the regression fit yield envelopes. The dashed lines represent a lower bound of the brittle failure envelope.
Figure 4.30: Coefficient of internal friction, $\mu$, versus temperature, for hollow cylinders made of aromatic epoxy with $M_c = 900$ grams/mol, tested at $\dot{\gamma}^{\text{oct}} = 0.028 \text{ min}^{-1}$ and varying temperatures. The solid symbols and error bars represent the slopes and standard deviation of the slopes in the yield envelopes of Figure 4.26.
Figure 4.31: Coefficient of internal friction, $\mu$, versus temperature, for Polycarbonate as reported by Homes et al.\textsuperscript{22}, PMMA as reported by Sternstein\textsuperscript{10}, and Epoxy as reported by Crawford and Lesser\textsuperscript{54}. 
Bauwens-Crowet, Bauwens and Homes’s work and Figure 4.31 show that μ increases as the temperature is decreased below the onset of the β transition in polycarbonate, which strongly supports our findings. From this, we believe that both the activation volumes of yield, v and Ω, and the coefficient of internal friction, μ, are dependent on temperature. However, further studies are needed to verify this.

We now want to calculate how v and Ω are affected by changes in temperature and $M_c$. To do this, we first make the assumption that μ decreases in a step manner as the temperature is increased above the upper limit of the β transition. For this we return to Figure 4.30, where we see that at 10°C and 21°C the coefficient of internal friction has an average value of μ=0.26, while at 50°C and 80°C there is an average value of μ=0.195. Additionally in a previous study, we showed that μ is independent of $M_c$. Therefore by substituting a value of μ=0.26 for all tests run at 0°C or below, and a value of μ=0.195 for all tests run above 20°C into equation (4.16), the compressive yield strengths of aromatic amine cured epoxies with varying $M_c$, measured over a range of strain rates and temperatures (see Figures 4.24, 4.32-4.34), can be used to calculate how both v and Ω are affected by both temperature and $M_c$ (see Figures 4.35-4.38). Please note that in this study we also calculated v and Ω, assuming that μ decreased linearly with increased temperature. Although the results of these calculations are not plotted, the same trends were observed as shown in Figures 4.35-4.38.

From Figures 4.35 and 4.36, we see that both v and Ω are unaffected by changing crosslink density. This combined with our previous findings that μ is unaffected by crosslink density, suggests that all of v, Ω and μ are independent of $M_c$. With regard to the
Figure 4.32: Compressive yield strength/temperature versus axial strain rate, for the aromatic amine cured epoxy with $M_c = 1840$ grams/mol and tested over a range of temperatures.
Figure 4.33: Compressive yield strength/temperature versus axial strain rate, for the aromatic amine cured epoxy with $M_c = 680$ grams/mol and tested over a range of temperatures.
Figure 4.34: Compressive yield strength/temperature versus axial strain rate, for the aromatic amine cured epoxy with \( M_c = 430 \) grams/mol and tested over a range of temperatures.
Figure 4.35: Shear activation volume for yield, $v$, versus molecular weight between crosslinks, for the aromatic system. $v$ was calculated from the compressive yield response in Figures 4.24, 4.32-4.34, using equation (4.16). In equation (4.16), a value of $\mu=0.26$ was used for all tests run at 0°C or below, and a value of $\mu=0.195$ was used for all tests run above 20°C.
Figure 4.36: Dilatational activation volume for yield, $\Omega$, versus molecular weight between crosslinks, for the aromatic system. $\Omega$ was calculated from the compressive yield response in Figures 4.24, 4.32-4.34, using equation (4.16). In equation (4.16), a value of $\mu=0.26$ was used for all tests run at $0^\circ$C or below, and a value of $\mu=0.195$ was used for all tests run above $20^\circ$C, and the following substitution was made: $v = \frac{\Omega}{\mu}$. 
Figure 4.37: Shear activation volume for yield, \( v \), versus temperature, for the aromatic epoxies. \( v \) was calculated from the compressive yield response in Figures 4.24, 4.32-4.34, using equation (4.16). In equation (4.16), a value of \( \mu = 0.26 \) was used for all tests run at 0°C or below, and a value of \( \mu = 0.195 \) was used for all tests run above 20°C.
Figure 4.38: Dilatational activation volume for yield, $\Omega$, versus temperature, for the aromatic epoxies. $\Omega$ was calculated from the compressive yield response in Figures 4.24, 4.32-4.34, using equation (4.16). In equation (4.16), a value of $\mu=0.26$ was used for all tests run at $0^\circ$C or below, and a value of $\mu=0.195$ was used for all tests run above $20^\circ$C, and the following substitution was made: $v = \frac{\Omega}{\mu}$. 
effect of temperature, Figure 4.37 shows that $v$ increases with temperature. This has also been shown by others\textsuperscript{57}. Figure 4.38 shows that $\Omega$ increases slightly with increasing temperature. Note that when $\mu$ was assumed to decrease linearly with increased temperature, that $\Omega$ remained unchanged with increased temperature. From the results of this and a previous papers\textsuperscript{23,56}, the manner in which $v$, $\Omega$ and $\mu$ are affected by testing conditions and molecular architecture is summarized in Table 4.2. However, additional studies are needed to understand the effect of temperature on the activation volumes of yield.

Table 4.2: Summary of the effect of testing conditions and molecular architecture on the activation volumes of yield, for aliphatic and aromatic amine cured epoxies.

<table>
<thead>
<tr>
<th>Variable</th>
<th>Increase Temperature</th>
<th>Increase Strain Rate</th>
<th>Increase $\sigma_m$</th>
<th>Increase $M_c$</th>
<th>Increase Backbone Stiffness / Intermolecular Interactions</th>
</tr>
</thead>
<tbody>
<tr>
<td>$v$</td>
<td>↑/unknown</td>
<td>no affect</td>
<td>no affect</td>
<td>no affect</td>
<td>unknown</td>
</tr>
<tr>
<td>$\Omega$</td>
<td>unknown</td>
<td>no affect</td>
<td>no affect</td>
<td>no affect</td>
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</tr>
<tr>
<td>$\mu$</td>
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<td>no affect</td>
<td>no affect</td>
<td>no affect</td>
<td>↑</td>
</tr>
</tbody>
</table>
4.5 Modification of a Generalized Model for Yield in Glassy Polymer Networks

In order to improve our phenomenological yield model for glassy polymer networks, it is first important to understand how equation (4.9) was developed. As section 4.2 describes, equation (4.9) was developed by simply generalizing equation (2.5 or rewritten as 4.4) and expressing it in the form of equation (2.1). Finally, the phenomenological model was extended to include molecular parameters ($M_c$ and $\phi$) by substituting equation (2.2) for $T_g$.

As previously stated, the application of equation (4.9) implies that the introduction of crosslinks into these polymers does not change activation volumes for shear, $\nu$, and dilation, $\Omega$, and hence the value for $\mu$. The results in section 4.4 of this thesis show that indeed $\nu$, $\Omega$ and $\mu$ are unaffected by changes in $M_c$. It is important to note, however, that $\nu$, $\Omega$ and $\mu$ probably all vary with temperature and backbone stiffness. Also equation (4.9) implies that changing $T_g$ is the same as changing $T$. Our findings in section 4.4 have shown this implication to be incorrect. In fact it was found that the effect of changing the testing temperature and $T_g$ of the these materials is better described by equation (4.13).

$$\sigma_y = \sigma_y^0 + \alpha(T - \beta T_g) \quad \text{for } T < T_g$$

(4.13)

Therefore, by expressing equation (2.5 or 4.4) in the form of equation (4.13), rather than equation (2.1), one obtains a more accurate expression for the yield strength of a glassy polymer in a generalized state of stress:
\[
\tau_\gamma^\text{oct} = \tau_\gamma^{\text{oct}_{0}}(\dot{\gamma}, \beta T_g) + \frac{R \beta T_g}{v(T, \phi)} \ln \left( \frac{\dot{\gamma}^\text{oct}}{\dot{\gamma}_r} \right) \\
+ \left( T - \beta T_g \right) \frac{R}{v(T, \phi)} \ln \left( \frac{\dot{\gamma}^\text{oct}}{\dot{\gamma}_r} \right) - \mu(T, \phi) \sigma_m 
\] 

(4.22)

where \( \tau_\gamma^{\text{oct}_{0}}(\dot{\gamma}, \beta T_g) \) represents \( \tau_\gamma^\text{oct} \) at a reference temperature, \( \beta T_g \) and some reference strain rate, \( \dot{\gamma}_r \). The second term on the right hand side of equation (4.22), \( \frac{R \beta T_g}{v(T, \phi)} \ln \left( \frac{\dot{\gamma}^\text{oct}}{\dot{\gamma}_r} \right) \), reflects the offset in \( \tau_\gamma^{\text{oct}_{0}} \) at the reference temperature, \( \beta T_g \), that results when testing at some strain rate, \( \dot{\gamma}^\text{oct} \), which differs from \( \dot{\gamma}_r \). The third term, \( \left( T - \beta T_g \right) \frac{R}{v(T, \phi)} \ln \left( \frac{\dot{\gamma}^\text{oct}}{\dot{\gamma}_r} \right) \), contains the linear dependence of \( \tau_\gamma^\text{oct} \) on \( T \) at the testing strain rate, \( \dot{\gamma}^\text{oct} \). The last term, \( \mu(T, \phi) \sigma_m \), describes the linear decrease in \( \tau_\gamma^{\text{oct}_{0}} \) as the hydrostatic stress is increased.

Consequently, equation (4.22) provides a general expression for predicting \( \tau_\gamma^\text{oct} \) for any given \( T, \dot{\gamma}^\text{oct} \), and state of stress. Note that both \( v(T, \phi) \) and \( \mu(T, \phi) \) are functions of temperature and backbone stiffness of the resin.

Finally, equation (4.22) can again be extended to include the Fox expression for \( T_g \) (equation 2.2) for crosslinked systems. For crosslinked resins, equation (4.22) takes the following form:
\[
\tau_{\gamma}^{\text{oct}} = \tau_{\gamma}^{\text{oct}}_0 \frac{\phi}{M_c} + \beta \left( T_{\gamma} + \frac{\phi}{M_c} \right) \frac{R}{v(T, \phi)} \ln \left( \frac{\dot{\gamma}}{\dot{\gamma}_r} \right)
\]

\[
+ \left( T - \beta \left( T_{\gamma} + \frac{\phi}{M_c} \right) \right) \frac{R}{v(T, \phi)} \ln \left( \frac{\dot{\gamma}_r}{\Gamma} \right) - \mu(T, \phi) \sigma_m
\]

Equation (4.23) allows for predicting how \( \tau_{\gamma}^{\text{oct}} \) will change, as \( M_c \) and \( \phi \) of a crosslinked thermoset is altered, in addition to the \( T, \dot{\gamma}^{\text{oct}} \), and stress state effects. Moreover, this model remains a "working model" in the sense that the parameters used in it can be readily determined from standard mechanical and thermal tests.

### 4.6 Comparison of Modified Model with Experimental Results

Using results from ASTM standard compression tests and thermal tests, shown in Figures 4.1, 4.18, 4.19 and 4.27, and inserting them into equation (4.23), \( \tau_{\gamma}^{\text{oct}} \) can be determined for any epoxy with a given \( M_c, \phi, T, \dot{\gamma}^{\text{oct}} \), and stress state. \( \tau_{\gamma}^{\text{oct}}_0 \) was calculated from the results in Figure 4.18 or 4.19, using the extrapolated compressive yield strength at \( \beta T_g \), \( \sigma_{\gamma c}^{\beta T_g} \), with \( \dot{\gamma}_r = .028 \) min\(^{-1} \) and the relationship:

\[
\tau_{\gamma}^{\text{oct}}_0 \frac{\phi}{M_c} = \frac{\sqrt{2}}{3} \sigma_{\gamma c}^{\beta T_g} - \frac{1}{3} \mu \sigma_{\gamma c}^{\beta T_g}
\]

\( v(T, \phi) \) in equation (4.23) was estimated to be 3.7 nm\(^3\) for the aromatic epoxies from Figure 4.27, and was taken to be 3.8 nm\(^3\) at 21°C for the aliphatic systems, as found in a previous study\(^{56} \). Values for \( T_{\gamma \infty} \) and \( \phi \) were obtained from the DSC data in Figure 4.1. The aliphatic system yields a value of \( \phi = 38.8 \) K kg/mol and \( T_{\gamma \infty} = 310 \) K, while the
aromatic system yields a value of \( \phi = 34.8 \text{ K kg/mol} \) and \( T_{\Gamma} = 358 \text{ K} \). \( \Gamma \) is calculated as follows:

\[
\Gamma = \frac{y_{\text{oct}}^\prime}{\exp\left(\frac{V_{\mu}}{R^\prime}\right)}
\]

(4.25)

where \( \alpha \) is calculated from Figures 4.18 and 4.19 using equation (4.13), and corrected to account for the octahedral shear stress. Finally, for the aromatic epoxies, \( \mu \) was determined from hollow cylinder tests (e.g., Figure 4.29 and 4.30). A value of \( \mu = 0.166 \) was used for the aliphatic systems at 21°C.

Figure 4.39 presents the yield strengths of hollow cylinders collapsed using equation (4.23), for the aliphatic epoxies with four different \( M_c \)'s and tested at three different strain rates, and the aromatic epoxy with \( M_c=900 \text{ grams/mol} \) tested over a range of temperatures. The model's reference yield envelope is plotted as a solid line, and the experimentally measured yield data for the aliphatic and aromatic epoxies are plotted as solid and hollow symbols, respectively. For both the aliphatic epoxies, equation (4.23) predicts the yield strength quite well over stress states ranging from uniaxial compression to biaxial tension, over three orders of magnitude of strain rates and a range of \( M_c \). However Figure 4.39 shows deviations when the aromatic yield strengths are collapse to those for the aliphatic epoxies. The deviations are due to the fact that \( \mu \) is higher for the aromatic epoxies than for the aliphatic epoxies, and \( \mu \) changes with temperature. Note that equation (4.23) does recognize this change in \( \mu \) with changing backbone structure and temperature, but we have made no attempt to adjust for the change in \( \mu \) in Figure 4.39. In Figure 4.39, only the yield
Figure 4.39: Octahedral shear yield stress versus hydrostatic stress, for hollow cylinders made of aliphatic epoxies with varying $M_c$ and tested over a range of octahedral shear strain rates, $\dot{\gamma}^{\text{oct}}$, and an aromatic epoxy with $M_c = 900$ grams/mol that was tested over a range of temperatures. The solid symbols represent the experimentally measured yield strengths that have been collapsed to the solid line, which represents the predicted yield response from equation (4.23).
strengths in pure shear were collapsed using equation (4.23), hence explaining the deviations.

### 4.7 Conclusion Regarding Single-Phase Epoxies

We conducted this study to more fundamentally investigate the yield and fracture response of glassy polymers subjected to constrained stress states. Our tests have elucidated the effects that stress state, strain rate, testing temperature, $M_c$ and backbone stiffness have on the yield response of these materials.

Our experiments showed that the yield response of glassy epoxy networks phenomenologically follows a modified von Mises yield criterion over the range of stress states, strain rates, temperatures, $M_c$ and backbones structures tested. Furthermore, changes in $\dot{\gamma}^{\text{oct}}$ and $M_c$, only affect $\tau_{y0}^{\text{oct}}$ as described by an Eyring type flow process. The coefficient of internal friction, $\mu$, is insensitive to changes in $\dot{\gamma}^{\text{oct}}$ and $M_c$ over the ranges tested.

However, it was found that changes in temperature and backbone structure (from aliphatic to aromatic) affect both $\tau_{y0}^{\text{oct}}$ and $\mu$. Note that due to the scatter in our yield data and the fact that the aromatic epoxies were brittle in uniaxial tension, it is difficult to make definitive statements regarding the changes in activation volumes with changing test temperature. However, our results suggest that the activation volumes are probably affected by the $\beta$ transition.

From our early work on single-phase epoxy networks, it was shown that the only affect that $M_c$ has on the yield strength of these resins is through a change in $T_g$. This yield
behavior can be accurately described by applying equation (2.5) to the octahedral plane and extending it to include the Fox Equation\(^8\) (equation 2.2). The resulting description of the yield model in equation (4.9) contains parameters which are related to the molecular architecture of the resin (e.g., \(T_{go}, M_c, \) and \(\phi\)) and parameters which can be readily determined from standard experiments.

The molecular origins of the yield model suggest that yielding in epoxy resins is a thermally activated process, whereby the epoxy is transformed from a glassy to a rubbery-like state at yield. Furthermore, resin crosslinking suppresses this transformation and can be directly correlated to an increase in the \(T_g\). In this sense, the \(T_g\) and the yield stress of the epoxy resin are intimately related. Before moving on, a disclaimer must be made at this point; Although equation (4.9) is based on Robertson’s model for yield\(^5\), which states that yield is governed by intramolecular forces which can be described by a thermally activated process where the backbone of the epoxy is transformed from a \textit{trans} to a \textit{gauche} conformation. We do not support the idea of glassy polymer yield being intramolecular in origin.

Equation. (4.9) was shown to accurately describe the yield response of these resins over a broad range of \(\dot{\gamma}\)’s and stress states, and over a small range of values of \(M_c\). However, when the model was used to predict the yield strength of aliphatic epoxies over a wide range of \(M_c\)’s, deficiencies were discovered. Further studies showed the source of the discrepancies between the model and experimental yield data for materials with low \(M_c\). In the derivation of equation (4.9), it was assumed that changing the \(T_g\) of epoxy resins has the same effect on the yield strength as a change in temperature. Further studies described in
Section 4.4.1 showed that the yield strength of these materials is actually affected more greatly by a change in testing temperature than it is by a $T_g$ change that is induced through a change in molecular weight between crosslinks. In hindsight this finding makes a lot of sense, as changing $T_g$ through a change in $M_c$ has been shown to have no effect on the backbone stiffness or packing density, while changing temperature definitely affects packing density and hence the intermolecular barriers of yield.

From this new understanding of the differing effect of changing $T_g$ and temperature on yield, combined with a more thorough investigation into the effects of stress state, strain rate, temperature, $M_c$ and backbone structure on the activation volumes of yield, equation (4.9) was modified. The new yield model, equation (4.23), more accurately predicts the yield strengths of both the aliphatic and aromatic epoxies, over stress states ranging from uniaxial compression to biaxial tension, over three orders of magnitude of strain rates, a $70^\circ C$ change in temperature, and a range of $M_c$ and backbones stiffness. However, the new model is rather cumbersome to use in practice.

In this study, we also measured the brittle failure strengths of epoxies with different molecular architectures that were tested in varying stress states, strain rates and temperatures. Although further studies are needed to fully understand the effects of molecular architecture and test conditions on the brittle fracture and the brittle-to-ductile transition in epoxy networks, it is clear that the effects can be significant. At this point it is not clear how the brittle-to-ductile transition is affected by $M_c$, backbone structure or testing temperature. However, there is strong evidence that the pressure dependence on fracture is
sensitive to these parameters. No attempt is made to address the mechanisms that govern the brittle response or the ductile/brittle transitions of these resins.
CHAPTER 5

RUBBER-MODIFIED EPOXIES

In this Section, we report the results from an experimental investigation into the three regimes of deformation that were described in Section 1.2. The work we present here is in line with much of the work done rubber-toughening community, in that the goal of our work is to better understand energy absorbing mechanisms that toughen materials. The distinguishing characteristic of this work is that we attempt to more quantitatively identify the effects of the energy absorbing mechanisms on the macroscopic behavior of the materials, by testing the materials in both confined and controlled stress states. This differs from the controlled, yet unconfined, tensile tests that are often run, and also differs from the highly confined, yet uncontrolled, fracture test that are performed. This work also differs from the majority of work in this field, that only qualitatively identifies the mechanisms of rubber-toughening.

We present results that describe the macroscopic yield/failure envelopes of aromatic amine cured EPON 828 epoxy networks, with 0%, 10%, and 20% CTBN rubber by weight. This particular system has been shown to increase the fracture of epoxy, see Figure 5.1. Furthermore as shown in Figure 5.2 for these rubber modified epoxies, the increase in fracture toughness due to the addition of rubber particles is associated with both particle cavitation and inelastic void growth. Therefore under controlled and confined stress states, we attempted to investigate both particle cavitation and inelastic void growth and the effect of these energy-absorbing mechanisms on the macroscopic
Figure 5.1: Fracture toughness measured from 3-point bend specimens versus temperature, for aromatic amine cured epoxy with 0\% and 10\%CTBN rubber by weight and $M_c=900$ grams/mol. These tests were performed by Emmett Crawford.
Figure 5.2: SEM micrographs of both the stress whitened and fast fractured surfaces from a 3-point bend specimen. The material is an aromatic amine cured epoxy with 10%CTBN rubber by weight and $M_c=900$ grams/mol. These micrographs were taken by Emmett Crawford.
yield behavior of these materials. The failure envelopes encompass stress states ranging from uniaxial compression to biaxial tension. Additional studies are conducted to determine the onset of significant irreversible deformation in the materials subjected to equal biaxial tension. The results from this investigation are then discussed in context to the models outlined in the Section 2.2 of this thesis.

The rubber-modified epoxies that were used in the hollow cylinders in this investigations have been described in detail in section 3.2.2 of this thesis. However for ease of reading, Table 3.4 has been reprinted below, describing each of the rubber-modified materials used in this study.

Table 5.1: Description of Rubber-Modified Epoxies

<table>
<thead>
<tr>
<th>Material Designation</th>
<th>M&lt;sub&gt;c&lt;/sub&gt; (grams/mol)</th>
<th>Rubber Concentration (weight %)</th>
<th>Particle Concentration (volume %)</th>
<th>Mean Particle Diameter (μm)</th>
<th>T&lt;sub&gt;g&lt;/sub&gt; (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>900</td>
<td>0</td>
<td>0</td>
<td>not applicable</td>
<td>124</td>
</tr>
<tr>
<td>B</td>
<td>900</td>
<td>10</td>
<td>13</td>
<td>1.7 ± 1.3</td>
<td>122</td>
</tr>
<tr>
<td>C</td>
<td>900</td>
<td>20</td>
<td>29</td>
<td>2.3 ± 0.8</td>
<td>119</td>
</tr>
<tr>
<td>D</td>
<td>900</td>
<td>20</td>
<td>25</td>
<td>3.1 ± 2.5</td>
<td>119</td>
</tr>
</tbody>
</table>
5.1 Macroscopic Yield Envelope: Regime III

Before we examine the yield behavior of rubber modified epoxies, the following should be noted. In the rubber-toughening community, it is more common for yield and failure strengths to be reported as a von Mises equivalent stress, $\sigma_e$, rather than the octahedral shear stress, $\tau^{\text{oct}}$, that is commonly reported for single-phase polymer systems. The von Mises equivalent stress, $\sigma_e$, is typically used to more familiarly compare the strength of materials in various stress states to the strength that is typically measured in uniaxial tension or compression test. The relationship between $\sigma_e$ and $\tau^{\text{oct}}$ is a simple scaling effect:

$$\sigma_e = \frac{3}{\sqrt{2}} \tau^{\text{oct}} \quad (5.1)$$

Plots of equivalent stress, $\sigma_e$ versus volume strain, $\varepsilon_v$, as measured from hollow cylinder tests, are shown in Figure 5.3, for epoxy with 0%, 10%, and 20% CTBN rubber by weight. In Figure 5.3a, we see that as pure epoxy(samples A) is subjected to stress states with an increasing dilatational component, the yield strength decreases and the failure mode changes from ductile yield to brittle fracture. From Figure 5.3, note that in the rubber modified systems (samples B, C, and D), full macroscopic yield is not always realized before the specimens fail. However, their strengths do nearly reach the yield envelopes extrapolated from the less demanding stress states. This suggests that significant localized yielding is occurring in these systems, and hence their change in failure mode is less evident.
Figure 5.3: von Mises equivalent stress versus volumetric strain, for hollow cylinders made of aromatic amine cured epoxies with $M_c=900$ grams/mol and various rubber content, and tested at $\dot{\gamma}_{oct} = 0.028 \text{ min}^{-1}$. The solid and dashed lines represent the ductile yield and brittle fracture envelopes, respectively. (a) Sample A: 0wt% CTBN rubber, (b) Sample B: 10wt% CTBN rubber, (c) Sample C: 20wt% CTBN rubber, and (d) Sample D: 20 wt% CTBN rubber.
Figure 5.3 continued.
Figure 5.3 continued.
Figure 5.3 continued.
Comparison of Figures 5.3a-5.3c illustrates the effect of rubber volume fraction on the yield behavior of epoxy over the range of stress states. These results show that the addition of rubber particles reduces the yield strength uniformly through the entire range of stress states, as can be described as follows:

\[
\sigma_e(f) = (1 - 1.32f)\sigma_e(0)
\]  

(5.2)

where \(\sigma_e(f)\) is the von Mises equivalent yield stress of samples with a volume fraction, \(f\), of rubber particles, and \(\sigma_e(0)\) is the von Mises equivalent yield stress of the matrix epoxy.

In the development of equation (5.2), samples A, B, C and D were assumed to contain \(f = 0.0, 0.13, 0.29\) and 0.25 volume fraction of rubber particles, as was measure from Figure 3.1 and is reported in Table 3.4. A similar comparison between Figures 5.3c and 5.3d (i.e., effect of particle size) shows that changing particle size does not significantly alter the yield behavior in the less demanding stress states. However, particle size does affect the ability of the samples to reach yield in the more demanding stress states, as the samples with large particles often failed at stresses below the yield envelope.

Figure 5.4 summarizes the hollow cylinder results, where the equivalent yield and fracture strengths of each sample are plotted versus hydrostatic stress, \(\sigma_m\). In this figure, the solid and hollow symbols represent macroscopic yield and brittle failure, and the solid and dashed lines represent the yield and brittle failure envelopes respectively. Figure 5.4 reconfirms the statements made previously about the effect of particle concentration, particle size and stress state on the yield behavior. Figure 5.4 also shows that brittle failures at strengths significantly below the materials’ yield envelopes only occurred in materials A (the unmodified resin) and D (25% vol -3.1 \(\mu\)m diameter particles). Since the resin with the
Figure 5.4: von Mises equivalent stress versus hydrostatic stress, for hollow cylinders made of rubber-modified epoxy with $M_c=900$ grams/mol, and tested at $\dot{\gamma}^{oct} = 0.028 \text{ min}^{-1}$. The solid symbols, hollow symbols, and lines represent ductile yield, brittle fracture, and the regression fit yield and fracture envelopes of samples A, B, C, and D.
large rubber particles tended to fail in a brittle manner at the same range of hydrostatic stresses as the unmodified resin, this indicates that the large rubber particles provided no significant toughening.

5.2 Comparison of Experimental Results to Yield Model Predictions

The normalized strengths for samples A, B, C, and D are presented in Figure 5.5, together with the predictions made by equation (2.11) assuming all of the particles cavitate (i.e., $f = \text{volume fraction of rubber}$). As described in section 2.2.2, equation (2.11) is a yield function, developed by Lazzeri and Bucknall, that describes the macroscopic yield behavior of porous epoxies over a range of stress states. The yield function considers macroscopic shear yielding and local inelastic void growth only and was introduced as follows:

$$
\Phi = \left( \frac{\sigma_e}{\sigma_0} \right)^2 + \frac{\mu_e \sigma_m}{\sigma_0} \left( 2 - \frac{\mu_e \sigma_m}{\sigma_0} \right) + 2f \cosh \frac{3\sigma_m}{2\sigma_0} - f^2 - 1 = 0
$$

where:

- $\sigma_e$ is the von Mises equivalent stress
- $\sigma_0$ is the yield stress in the absence of hydrostatic stress
- $\sigma_m$ is hydrostatic stress
- $\mu_e$ is the tensile equivalent coefficient of internal friction, where $\mu_e = \frac{3}{\sqrt{2}} \mu$
- $f$ is the volume fraction of pores dispersed in the matrix.
In Figure 5.5, the solid and hollow symbols and dashed lines represent the experimentally measured yield and brittle strengths and yield envelopes of the samples, normalized to the pure shear yield strength of the unmodified epoxy. The strengths of samples A which failed by a brittle mode have been omitted from the plot to avoid confusion. The solid lines are the predictions from equation (2.1) for epoxy with $\mu_e = .55$ and $f = 0.0, 0.13, 0.25$ and 0.29 respectively.

From Figure 5.5, we first see that equation (2.1) does predict the yield envelope of the pure epoxy. This is expected, because when $f=0$, equation (2.1) reduces to a modified von Mises yield function, which has been shown to describe the yield behavior of epoxies. However, at all nonzero concentrations of rubber, significant deviations exist between the measured yield data and that predicted by equation (2.1). The discrepancies between the measured and predicted yield envelopes can be summarized by two main differences.

The first noticeable difference is that equation (2.1) describes a nonlinear relationship between the deviatoric and hydrostatic stress at all nonzero void fractions, while the experimental data show a linear behavior. One possible reason for this difference is that a significant fraction of the rubber particles may not have cavitated. Even though the models for rubber particle cavitation, described in Section 2.2.1 and plotted Figure 2.1, predict that the rubber particle cavitation should have occurred in the more dilatational stress states, no significant rubber particle cavitation nor inelastic void growth was observed in the failed samples. This can be seen by comparing the cryo-fractured surfaces of samples C loaded in uniaxial compression, pure shear and biaxial tension(see Figure 5.6). From
Figure 5.5: Comparison of the yield envelopes to the Lazzeri-Bucknall yield function for Epoxy with 0%, 10% and 20% CTBN rubber by weight. The solid and hollow symbols and dashed lines represent the actual yield and brittle strengths and yield envelopes of samples A, B, C, and D. The solid lines represent equation (2.11)'s predictions for $f=0$, 0.13, 0.25 and 0.29.
Figure 5.6: SEM micrographs of cryo-fractured samples C, loaded in different stress states: 5.6a) Unstressed, 5.6b) Uniaxial Compression to Yield, 5.6c) Pure Shear to Yield, and 5.6d) Biaxial Tension to 41 MPa.
Figure 5.6, note that the rubber particle are more visible in uniaxial compression, pure shear and biaxial tension, when compared to the undeformed sample. This suggests that the shear stress causes these the rubber particles to be more visible, and that the visibility of the rubber particle is not solid evidence of particle cavitation or inelastic void growth. Therefore we believe that too little cavitation and/or inelastic void growth occurred in the materials over the range of stress states tested to accurately evaluate equation (2.11). This raises a question about the applicability of the rubber physical properties used in Figure 2.1, for our materials.

The second difference relates to discrepancies between the experimental data and model predictions in the stress states with low or even negative levels of hydrostatic stress. It is acknowledged that at negative hydrostatic stress levels, the particles will not cavitate and may take significant hydrostatic loads. Hence, equation (2.11) should predict a lower bound in this regime, since the model as we prescribe it herein assumes that voids are present as opposed to rubber particles. Under this condition, equation (2.11) would approximate inelastic void collapse to be unbounded in a fashion analogous to inelastic void growth. However, the yield strengths are below the model predictions, which suggest that other aspects not accounted for in the model (e.g., particle interactions, polydispersity in spacing, etc.) may be operative.

Along the same line of thinking, we do recognize that at all negative hydrostatic stresses, particle cavitation and inelastic void growth are not possible. Therefore in a new plot (Figure 5.7), we have again plotted the results of Figure 5.5. However this time in the stress states with a negative hydrostatic component of stress, a modified von Mises yield
Figure 5.7: Comparison of the yield envelopes to the Lazzeri-Bucknall yield function for Epoxy with 0%, 10% and 20% CTBN rubber by weight. The solid and hollow symbols and dashed lines represent the actual yield and brittle strengths and yield envelopes of samples A, B, C, and D. The solid lines represent equation (2.11)’s predictions for $f=0, 0.13, 0.25$ and 0.29. Note that in the stress states with a negative hydrostatic component of stress, the solid lines were calculated using a reduced yield strength in equation (2.11) with $\mu_e = .55$ and $f = 0.0$, regardless of the volume fraction of rubber particles.
criteria with $\mu_e = .55$ was used to calculate the solid lines Figure 5.7. This was done, because Professor’s Lazzeri and Bucknall felt that Figure 5.7 would more reasonably describe the predictions of their model.

To further illustrate this point, Figure 5.8 shows how the reported compressive yield strengths of several rubber-modified polymer systems$^{39,43,59-61}$ are affected by the addition of rubber and hollow latex particles, as well as that predicted by equation (2.11) for uniaxial compression, pure shear and uniaxial tension. Note that according to equation (2.11), the relative decrease in yield strength with increased rubber particle or void volume fraction is the same in uniaxial compression as in pure shear. From Figure 5.8, we see that equation (2.11) over-predicts the compressive yield strengths as a function of particle concentration for most of the reported materials, regardless of whether the model is used in compression, pure shear or tension. Decreases in yield strength with increased void or rubber content that are more in line with equation (2.11)’s predictions have been reported for core-shell rubber particles$^{39}$ and for hollow latex particles with a diameters of 0.4$\mu$m and 1.0$\mu$m. However for these materials, the reported sizes of the particles included the hard shells of the particles. Therefore, we believe that the effective volume fraction of rubber particles or voids is lower than reported, because the hard-shells of the particles do not behave as soft rubber inclusions or as voids.

With regard to the effect of hydrostatic stress on the yield envelope of rubber-modified polymers, Sultan and McGarry have also tested hollow cylinders of pure and rubber modified epoxies in stress states ranging from uniaxial compression to biaxial
Figure 5.8: Comparison of the reported yield strengths of various rubber-modified polymers to the Lazzeri-Bucknall yield function (equation 2.11), as a function of particle volume fraction. The solid symbols represent the reported yield strengths\(^{39,43,59-61}\) and the solid lines represent the model predictions for uniaxial compression, pure shear and uniaxial tension.
tension. Their results have been replotted in Figure 5.9. They reported that the yield behavior of both the pure epoxy and the rubber-modified epoxy with particles of 0.04 μm in diameter followed a modified von Mises type yield behavior, over all stress states tested. Additionally, they noted that the only affect of adding the rubber particles to the epoxy was a decrease in \( \tau_{y0}^{\text{oct}} \), as \( \mu \) remained constant for both materials at 0.175. These results are in line with our own, in that Sultan and McGarry reported that the rubber-modified samples with particles of 0.04 μm in diameter did not whiten in the highly confined stress states. However with regard to the rubber-modified epoxies with larger rubber particles, Sultan and McGarry reported that the samples whitened in the more confined stress states. This whitening was attributed to particle cavitation and matrix stretching in the case of biaxial tension. So although \( \mu \) remained constant at 0.175 in the stress states with low or negative levels of hydrostatic stress, \( \mu \) was reported to increase to 0.210 for samples that whitened in the more highly confined stress states. These results support the model of Lazzeri and Bucknall, and suggest that inelastic void growth does cause a downward curvature in the failure envelope of rubber-modified epoxies, if the rubber particles cavitate. However, the scatter in the yield strengths of the rubber modified epoxies, reported in Figure 5.9, makes it hard to draw any solid conclusions.
Figure 5.9: von Mises equivalent yield stress versus hydrostatic stress, for hollow cylinders made of pure and rubber-modified epoxy. This Figure has been replotted from the work of Sultan and McGarry.11
5.3 Energy Absorbing Characteristics Prior to Macroscopic Yield: Regime II

Selected tests were conducted to quantitatively assess the energy absorbing characteristics that are activated before gross yielding occurs in the modified epoxies. The tests involved monotonically loading and unloading a series of hollow cylinders in equal biaxial tension to a range of stress levels prior to failure. Differences in stiffness, irreversible work, and damage morphology were monitored.

A plot of the axial stress, $\sigma_a$, versus axial strain, $\varepsilon_a$, for samples C loaded and unloaded in biaxial tension is shown in Figure 5.10. Up to a threshold stress level of $\sigma_a \approx 19\text{MPa}$, the deformation is elastic. Just beyond this stress level, a change in the loading stiffness is observed, and the deformation process becomes increasingly irreversible. This irreversibility is observed in the hysteresis produced between the loading and unloading curves. In Figure 5.11, the SEM micrographs of samples stressed to various levels shows the changes in damage morphology at different stress levels. Although the hysteresis curves indicate that approximately 19 MPa marks a threshold for significant increases in irreversibility, the micrographs in Figure 5.11 show no evidence that 19 MPa marks the onset of significant particle cavitation or inelastic void growth. Observations of other mechanisms are inconclusive. One thing that is apparent from Figure 5.11 is that even if the particles are cavitated, significant inelastic void growth is not observed at any stress level.

A second series of tests were conducted on the system with much larger particles (samples D). The biaxial stress-strain hysteresis curves for these tests are given in Figure 5.12. The irreversible work done to rubber-modified samples C and D loaded and unloaded
Figure 5.10: Axial stress versus axial strain for samples C, loaded and unloaded in biaxial tension to different maximum stress levels: $\sigma_a = 0, 16, 31, \text{ and } 40 \text{ MPa.}$
Figure 5.11: SEM micrographs of cryo-fractured samples C, loaded and unloaded in biaxial tension to different maximum stress levels: a) \( \sigma_a = 0 \) MPa, b) \( \sigma_a = 16 \) MPa, c) \( \sigma_a = 31 \) MPa, and d) \( \sigma_a = 41 \) MPa.
Figure 5.12: Axial stress versus axial strain for samples D, loaded and unloaded in biaxial tension to different maximum stress levels: \( s_a = 0, 16, 31, \) and 41 MPa.
in biaxial tension, $w_i$, was calculated from the hysteresis of Figures 5.10 and 5.12. In Figure 5.13, $w_i$ is plotted versus the maximum $\sigma_a$ for both samples C and D. Note that in biaxial tension, $\sigma_a$ is equal to $\sigma_h$, $\varepsilon_a$ is equal to $\varepsilon_h$, and $w_i$ is calculated by:

$$w_i = 2 \int_{0}^{\varepsilon_f} \sigma_a \, d\varepsilon_a$$

where $\varepsilon_f$ is the axial strain after a full loading and unloading cycle. Figure 5.12 shows that in biaxial tension, only above the threshold stress of $\sigma_a \approx 19\text{MPa}$ is significant irreversible work done to samples C and D. Note that the irreversible works plotted in Figure 5.13 are measures of the total energy dissipated.

Again Figure 5.13 shows that approximately 19 MPa marks the threshold for significant increases in irreversibility in both samples C and D. This suggests that the threshold stress is not associated with particle cavitation, since the cavitation stress is dependent on particle size$^{11, 31, 35, 37, 39}$. Consequently, this threshold must be associated with the onset of irreversible deformation of the matrix. Additionally, since no significant inelastic void growth is observed in Figure 5.11, we believe that the threshold stress and the irreversibility are primarily associated with other mechanisms (e.g. localized shear yielding), rather than particle cavitation or inelastic void growth. However, further studies are required to verify this.
Figure 5.13: Irreversible work versus maximum axial stress, for samples C and D loaded and unloaded in biaxial tension to different maximum axial stress levels.
5.4 Elastic Properties: Regime I

In Section 1.2 of this thesis, we described Regime I in the deformation of rubber modified epoxies as the linear elastic/viscoelastic regime, where both components of the material and the interface between them are intact. In this regime, the composite properties (e.g. density, stiffness, etc.) are well described by current micromechanics models\(^1\)\(^-\)\(^3\). To support these statements, in this section we both measure and calculate the effect of rubber particle on the bulk modulus of rubber-modified epoxies.

The bulk moduli of pure aromatic amine cured epoxy with \(M_c=900\) grams/mol, pure CTBN 1300X8 rubber, and the rubber-modified epoxy with 21% CTBN rubber by volume were measured using a GNOMIX Pressure-Volume-Temperature (PVT) apparatus. A schematic of the PVT apparatus is shown in Figure 5.14. To measure the bulk moduli of these materials, the samples were placed in a chamber filled with mercury and varying amounts of pressure were applied with a hand pump. The LVDT located at the bottom of the chamber measured the change in volume of the sample chamber at the different applied pressures. A plot of the volume strain of the sample, \(\varepsilon_v\), at the different applied pressures is shown in Figure 5.15. Note that the mercury in the chamber is considered to be incompressible. Therefore all of the volume change of the chamber is assumed to be due to the sample. From the slopes of the of the pressure versus \(\varepsilon_v\) plots in Figure 5.15, the bulk moduli of each of the samples was calculated. At room temperature, the bulk modulus of the pure aromatic amine cured epoxy with \(M_c=900\) grams/mol was 5.1 GPa, of the pure CTBN 1300X8 rubber was 2.6 GPa, and of the rubber-modified epoxy with 21% CTBN rubber by volume was 4.46 GPa.
Figure 5.14: Schematic of the GNOMIX Pressure-Volume-Temperature (PVT) apparatus, that was used to measure the bulk moduli of samples.
Figure 5.15: Applied pressure versus volume strain, for pure aromatic amine cured epoxy with $M_c=900$ grams/mol, pure CTBN 1300X8 rubber, and the rubber-modified epoxy with 21% CTBN rubber by volume, as measured using a GNOMIX Pressure-Volume-Temperature (PVT) apparatus.
To calculate the effect adding rubber particles to an epoxy matrix, Christensen's model\(^2\) for semi-dilute spherical inclusions was used:

\[
K = K_m + \frac{c(K_i - K_m)}{1 + \frac{(1-c)(K_i - K_m)}{K_m + \frac{4}{3} G_m}}
\]  

(5.4)

where \(K\) is the bulk modulus of the composite, \(K_m\) is the bulk modulus of the matrix, \(K_i\) is the bulk modulus of the spherical inclusion, \(c\) is the concentration of inclusions, and \(G_m\) is the shear modulus of the matrix. In the calculation of the predicted bulk modulus of the rubber-modified epoxy, equation (5.4) was used along with \(K_m=5.1\) GPa, \(K_i=2.6\) GPa, \(c=0.21\) and \(G_m=2.1\)GPa. Note that the rubber modified epoxy was cast between in a test tube and not spun cast. Therefore the volume fraction of rubber particles was very near that of the volume fraction of rubber added to the epoxy. \(G_m\) was calculated from tensile tests using both axial and transverse extensometers. Using equation (5.4), the bulk moduli of the rubber modified epoxy was predicted to be \(K=4.4\) GPa. The is very close to the \(K=4.46\) GPa that was measured in the PVT apparatus. The accuracy with which equation (5.4), as well as other similar models\(^1,3\) can predict the elastic properties of these composites suggests that the important work with regard to rubber modified epoxies needs to focus on understanding Regimes II and III of deformation.

### 5.5 Conclusions Regarding Rubber Modified-Epoxies

Biaxial testing of thin-walled hollow cylinders showed that the addition of rubber particles to epoxy: suppresses brittle failure in the more dilatational stress states and
decreases the yield strength of the epoxy uniformly over stress states ranging from uniaxial compression to biaxial tension, as described by equation (5.2). Particle size was found to have no significant effect on the yield behavior. Comparison between the measured yield envelopes with that of a recently published model based on a plastic porous media showed deviations. The first deviation is that the model predicts a curvature in the relationship between the deviatoric and hydrostatic stress, while the experimental results show a linear relation. This deviation is believed to be caused by a lack of significant particle cavitation and inelastic void growth over the ranges of stress states tested, and is not believed to be a downfall of the model. The overprediction of the yield strength in the less demanding stress states remains to be solved.

Separate studies were performed to quantitatively assess the energy absorption that occurs prior to macroscopic yield in rubber-modified epoxy tested in equal biaxial tension. The biaxial tests, revealed a threshold stress that is independent of particle size. Above this threshold stress, the stiffness of the rubber-modified resin decreases and deformation becomes increasingly irreversible. Morphological studies complimented the biaxial tests, showing that neither the threshold stress nor the irreversibility is associated with the onset of particle cavitation or inelastic void growth. Further studies are required to verify the origins of the irreversibility. Also it is believed that more sensitive methods for measuring inelastic void growth should be developed and utilized.
CHAPTER 6

VOIDED EPOXIES

This Chapter reports the results from an experimental investigation into the yield and fracture behavior of microvoided epoxies subjected to multiaxial states of stress. We present results that describe how the compressive yield strength of epoxies is decreased by the addition of voids. Additional studies are conducted describing the macroscopic yield/failure envelopes of epoxy networks, with 4% and 28% voids by volume. The failure envelopes encompass stress states ranging from uniaxial compression to biaxial tension. Finally, 3-point bend fracture tests are conducted to show how the presence of voids affects the fracture toughness of epoxies and the damage morphology of the fractured specimens. The results from this investigation are then discussed in context to the cavitation viewpoints and models outlined in Section 2.2.

6.1 Effect of Void Concentration on Compressive Yield Strength

As previously described in Chapter 3, Figure 3.3 shows the SEM micrographs of the voided compression samples, along with the volume fraction of voids(f), weight percent propylbenzene added, T_g’s, and particle size distributions. Table 6.1 summarizes this information and also reports the compressive yield strengths of the voided epoxies at 20°C and 30°C. In order to isolate the effects that the void fraction has on the macroscopic yield behavior of the epoxies, it was first necessary to determine how the yield strength was
Table 6.1: Description of voided epoxies used in the compression tests.

<table>
<thead>
<tr>
<th>Material Designation in Figure 3</th>
<th>( T_g ) (^{\circ}\text{C} )</th>
<th>weight % solvent (wt%)</th>
<th>volume % voids (vol%)</th>
<th>Mean Void Diameter (µm)</th>
<th>( \sigma_y ) @20(^{\circ}\text{C}) (\text{MPa})</th>
<th>( \sigma_y ) @30(^{\circ}\text{C}) (\text{MPa})</th>
</tr>
</thead>
<tbody>
<tr>
<td>a)</td>
<td>49.5</td>
<td>17</td>
<td>1.7</td>
<td>1.7 ± 0.5</td>
<td>45.2</td>
<td>35.6</td>
</tr>
<tr>
<td>b)</td>
<td>49.5</td>
<td>18</td>
<td>6.4</td>
<td>2.1 ± 0.3</td>
<td>43.9</td>
<td>37.0</td>
</tr>
<tr>
<td>c)</td>
<td>48.3</td>
<td>19</td>
<td>7.7</td>
<td>2.4 ± 0.5</td>
<td>42.2</td>
<td>35.5</td>
</tr>
<tr>
<td>d)</td>
<td>48.6</td>
<td>19</td>
<td>8.7</td>
<td>2.4 ± 0.4</td>
<td>41.0</td>
<td>34.3</td>
</tr>
<tr>
<td>e)</td>
<td>53.0</td>
<td>19</td>
<td>13.9</td>
<td>3.2 ± 0.8</td>
<td>40.2</td>
<td>34.3</td>
</tr>
<tr>
<td>f)</td>
<td>50.4</td>
<td>20</td>
<td>22.2</td>
<td>4.3 ± 1.2</td>
<td>36.8</td>
<td>32.8</td>
</tr>
<tr>
<td>g)</td>
<td>52.5</td>
<td>23</td>
<td>24.2</td>
<td>4.2 ± 1.0</td>
<td>36.9</td>
<td>32.7</td>
</tr>
<tr>
<td>h)</td>
<td>52.6</td>
<td>26</td>
<td>26.6</td>
<td>4.0 ± 1.0</td>
<td>37.2</td>
<td>31.5</td>
</tr>
<tr>
<td>i)</td>
<td>52.0</td>
<td>26</td>
<td>26.5</td>
<td>5.3 ± 1.2</td>
<td>33.4</td>
<td>29.4</td>
</tr>
<tr>
<td>j)</td>
<td>52.3</td>
<td>29</td>
<td>32.0</td>
<td>4.7 ± 1.2</td>
<td>34.1</td>
<td>28.2</td>
</tr>
<tr>
<td>k)</td>
<td>52.8</td>
<td>29</td>
<td>32.4</td>
<td>4.4 ± 1.3</td>
<td>31.4</td>
<td>28.3</td>
</tr>
</tbody>
</table>
reduced by the introduction of the solvent. Table 6.1 clearly shows that the samples with different void fractions also have different Tg's. This indicates that different concentrations of residual solvent remained in the matrix. To see how the yield strength is affect by void concentration only, we had to compare the yield strengths of the voided materials to the yield strengths of non-voided materials with the same Tg's. Therefore we measured the compressive yield strength of the epoxies that were swelled with varying amounts of propylbenzene, over a range of temperatures (see Figure 6.1). From Figure 6.1, we see that the yield strength of epoxy decreases with both increasing test temperature and solvent content or decreasing Tg.

In Sections 2.1 and 4.1, we show that the yield strength, \( \sigma_y \), of a series of aliphatic amine cured epoxies could be described by the following equation:

\[
\sigma_y = \sigma_y^{Tg} + \alpha(T - Tg) \quad \text{for} \ T < Tg
\]

(2.1)

where \( \sigma_y^{Tg} \) represents the yield stress at Tg, and \( \alpha \) is a negative term that describes the linear increase in \( \sigma_y \) as T is decreased below Tg. Equation (2.1) predicts that changing Tg has the same effect on yield as changing temperature. In our previous study, we had changed Tg though a change in molecular weight between crosslinks, \( M_c \). However, we later found that changing Tg in this manner did not have the same effect on \( \sigma_y \) as changing temperature. This difference is believed to be due to the following; Decreasing \( M_c \) increases Tg by increasing the intramolecular energy barrier, while changing temperature primarily changes the intermolecular energy barrier.
Figure 6.1: Compressive yield strength versus temperature, for EPON 828 cured with AEP and swelled with 0%, 5%, 9% and 13% propylbenzene by weight. Tests were conducted at an axial strain rate of 0.1 mm/mm/min and over a range of temperatures.
However when a material is swelled with a solvent, we believe that the $T_g$ is changed primarily through a change in the intermolecular energy barrier, similar to a change in temperature. Hence equation (2.1) should more accurately describe the behavior of these swelled materials. To test this, Figure 6.2 shows the compressive yield strengths from the swelled epoxies versus $\Delta T$, the difference between the testing temperature, $T$, and $T_g$.

$$\Delta T = (T - T_g) \quad (4.1)$$

In Figure 6.2, the compressive yield strengths of the swelled epoxies all collapse to a single curve, when compared at the same temperature shift below $T_g$, i.e. constant $\Delta T$. This $\Delta T$ dependence is described by equation (2.1) and suggests that with regard to yield strength, the effect of changing $T_g$ by swelling the epoxy is the same as changing temperature. There is a possible exception with regard to the pure epoxy, as the yield strengths of the pure epoxy tend to deviate from the others at lower temperatures. However, this deviation may be expected, as the pure epoxy has different intermolecular interactions than the swelled materials.

In Figure 6.2, the solid line represents the experimental fit of the swelled epoxy yield data to equation (2.1), with $\sigma_y^{T_g} = 29.4$ MPa and $\alpha = -0.75$ MPa/°C. Note that only the yield strengths of the swelled epoxies were fit to equation (2.1). In Figure 6.2, the yield strength of several of the voided epoxies are also plotted, so that the yield strengths of the voided epoxies can be compared to the non-voided/swelled epoxies that were tested at the same temperature shift below $T_g$. 

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Figure 6.2: Compressive yield strength versus $T-T_g$. The solid symbols represent EPON 828 cured with AEP and swelled with 0%, 5%, 9% and 13% propylbenzene by weight. The solid line is the linear regression fit of the yield strengths of the swelled epoxies. The hollow symbol represent the yield strengths of the voided epoxies with different volume fractions of voids($f$) that were tested at 20°C and 30°C and an axial strain rate of 0.1 mm/mm/min.
In Figure 6.3, the compressive yield strengths of the voided epoxies, normalized by the yield strength of the swelled epoxies tested at the same temperature shift below \( T_g \), how the reported compressive yield strength of epoxy is affected by the addition of hollow latex particles\(^{39}\), as well as that predicted by equation (2.11) for uniaxial compression, pure shear and uniaxial tension. From Figure 6.3, we see that equation (2.11) slightly over-predicts the compressive yield strengths as a function of void concentration for our voided epoxies tested at 20°C and more seriously for the epoxies with hollow latex particles of 15\( \mu m \) and 40\( \mu m \) in diameter. Decreases in yield strength for our voided epoxies tested at 30°C and the epoxies with hollow latex particles of 0.4\( \mu m \) and 1.0\( \mu m \) in diameter are more in line with equation (2.11)'s predictions. However at 30°C our voided epoxies are approaching their \( T_g \)'s, and hence equation (2.1) may not be as accurate at this higher temperature. As for the epoxies with the 0.4\( \mu m \) and 1.0\( \mu m \) hollow latex particles, the reported sizes of the particles included the hard shells of the particles. Therefore, we believe that the effective volume fraction of voids is lower than reported, because the hard-shells of the latex particles do not behave as voids.
Figure 6.3: Comparison of the normalized compressive yield strengths of the voided epoxies to the Lazzeri-Bucknall yield function (equation 1), as a function of particle volume fraction. The solid and hollow symbols represent the normalized compressive yield strengths of our voided epoxies and Pearson's results for epoxies modified with hollow latex particles\textsuperscript{39}, respectively. The lines represent the Lazzeri-Bucknall model predictions for uniaxial compression, pure shear and uniaxial tension (assuming $\mu_e=0.39$).
6.2 Macroscopic Yield Envelope

Figure 6.4 summarizes the hollow cylinder results for the hexane-voided epoxy, where the von Mises equivalent yield strengths of each sample are plotted versus hydrostatic stress, $\sigma_m$. The morphology of these samples is shown in Figure 3.2b. First it should be noted that the hexane-voided hollow cylinders were tested at 60°C to suppress brittle fracture and promote inelastic void growth by reducing the yield strength of the matrix. This was needed since the voided cylinders failed by a brittle mode at room temperature. In Figure 6.4, the yield envelope indicated no nonlinearity in the relationship between $\sigma_e$ and $\sigma_m$. These findings do not contradict the predictions of equation (2.11), as perhaps the 4% voids by volume is too low to measure any non-linearity in the yield envelope.

In an attempt to more thoroughly evaluate equation (2.11), we then tested propylbenzene-modified hollow cylinders with smaller voids and a much higher concentration of 28% voids by volume. The morphology of these samples is shown in Figure 3.2d. Figure 6.5 summarizes the hollow cylinder results for these propylbenzene-voided epoxies, where the von Mises equivalent yield and fracture strengths of each sample are plotted versus hydrostatic stress, $\sigma_m$. The solid and hollow symbols represent macroscopic yield and brittle failure, respectively. In the propylbenzene-voided epoxies, there is again no sign of a downward curvature in the relationship between the von Mises yield stress and $\sigma_m$. However for a material with 28% voids by volume, equation (2.11) does predict significant nonlinearity in the relationship between $\sigma_e$ and $\sigma_m$. The deviation between our measured yield envelope and that predicted by equation (2.11) can be
Figure 6.4: von Mises equivalent yield stress versus hydrostatic stress, for hollow cylinders made of EPON 825 cured with AEP and hexane-modified with 4% voids by volume. The cylinders were tested at 60°C and $\dot{\gamma}^\text{oct} = 0.028 \text{ min}^{-1}$. 

\[ \sigma_c (\text{MPa}) \] 
\[ \sigma_m (\text{MPa}) \]
Figure 6.5: von Mises equivalent stress versus hydrostatic stress, for hollow cylinders made of EPON 828 cured with AEP and propylbenzene-modified with 28% voids by volume. The solid and hollow symbols represent ductile yield and brittle failure, respectively. The cylinders were tested at 20°C and $\dot{\gamma}^{\text{oct}} = 0.028 \text{ min}^{-1}$. 
explained from the SEM micrographs of the hollow cylinders that are shown in Figure 6.6. These micrographs show no sign of significant inelastic void growth in the sample that was loaded in biaxial tension as compared to the sample loaded in uniaxial compression. Without inelastic void growth, the downward curvature in the relationship between $\sigma_e$ and $\sigma_m$ should not be measured, as the derivation of equation (2.11) describes a kinematically admissible solution that includes inelastic void growth. However, the reason that inelastic void growth was not observed in these materials may be because our method of measuring inelastic void growth, electron microscopy, is not sensitive enough.
Figure 6.6: SEM micrographs of cryofractured hollow cylinders made of EPON 828 cured with AEP and propylbenzene-modified with 28% voids by volume, that were loaded in different stress states: a) Uniaxial compression to yield, b) Biaxial tension to yield.
6.3 3-Point Bend Fracture Studies

In Table 6.2, the glass transition temperature and mechanical properties of the pure and voided 3-point bend specimens are reported. The morphology of the voided fracture samples is shown if Figures 3.2a) and 3.2c). By comparing the hexane-modified samples with 7% voids to the unmodified EPON 825 epoxy cured with AEP, one first notes that the fracture toughness is slightly higher for the voided material. However, the \( T_g \) of the hexane voided epoxy is lower than that of the unmodified epoxy. Therefore to obtain a better understanding of the effect of the addition of voids, in Figure 6.7 the fracture toughness' of both the voided and unmodified epoxies are plotted versus \( \Delta T \). Figure 6.7 shows that when compared at the same temperature shift below \( T_g \), that the fracture toughness of the voided epoxy is slightly below that of the unmodified epoxy. This suggests that the increased toughness of the voided epoxy is not due to the presence of voids, but is a consequence of the swelled and hence more ductile matrix.

Next, we compare the fracture toughness of the propylbenzene-modified samples with 32% voids by volume to that of the unmodified EPON 828 epoxy cured with AEP (see Table 6.2). In this case, the fracture toughness of the voided epoxy is significantly lower than that of the unmodified epoxy. Although it is not reported here, the toughness of the epoxy swelled with propylbenzene was also higher than that of the voided material. We then studied the fracture surface of the propylbenzene-modified samples with 32% voids that had been fractured at different temperatures (see Figure 6.8). The load deflection curves for the 3-point bend tests are plotted in Figure 6.9. Note that brittle fracture was observed in the voided samples at 21°C, while ductile fracture was observed at 50°C.
Table 6.2: Mechanical properties of the pure and voided epoxies used in fracture study.

<table>
<thead>
<tr>
<th>Material Designation</th>
<th>$T_g$ (°C)</th>
<th>$E @ 20^\circ C$ (GPa)</th>
<th>$\sigma_y c@20^\circ C$ (MPa)</th>
<th>$K_{lc} @20^\circ C$ (MPa m$^{1/2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EPON825/AEP</td>
<td>126</td>
<td>2.8</td>
<td>90</td>
<td>1.5</td>
</tr>
<tr>
<td>EPON825/AEP w/ 17% hexane</td>
<td>93</td>
<td>2.3</td>
<td>76</td>
<td>1.7</td>
</tr>
<tr>
<td>EPON828/AEP</td>
<td>125</td>
<td>2.9</td>
<td>89</td>
<td>1.54 ± 0.04</td>
</tr>
<tr>
<td>EPON828/AEP w/ 29% propylbenzene</td>
<td>52</td>
<td>1.2</td>
<td>31</td>
<td>1.15 ± 0.07</td>
</tr>
</tbody>
</table>
Figure 6.7: Fracture toughness as measured from 3-point bend tests versus $T-T_g$, for both unmodified and 7% hexane-voided EPON 825 cured with AEP. The unmodified samples were tested over a range of temperatures, while the voided samples were tested at 20°C.
Figure 6.8: SEM micrographs of fracture surfaces, from 3-point bend samples of EPON 828 cured with AEP and propylbenzene-modified with 32% voids by volume, that were fractured at different temperatures. a) liquid nitrogen temperature, b) 20°C, c) 50°C.
Figure 6.9: Load versus deflection curves from 3-point bend samples of unmodified and 32% propylbenzene-voided EPON 828 cured with AEP, that were tested at different temperatures.
No whitened zone in front of the crack tip was observed at either temperature. Figure 6.8 shows that no significant amount of inelastic void growth was observed on the 3-point bend fracture surfaces of the samples tested at 21°C or 50°C, as compared to the cryfractured sample. In fact only a shape change is observed in the voids.

These findings contradict much of the previously published work\textsuperscript{39,48,49}, which showed that the addition of microvoids to a matrix significantly toughened the material. Furthermore in our study, the reported energy absorbing mechanism of inelastic void growth was not observed. In fact our findings support the argument that epoxy resin containing holes is a very poor material\textsuperscript{50,51}. However, it is important to note that for all of our hollow cylinder and 3-point bend fracture toughness tests, the epoxies either contained very large voids or a very high concentration of voids. Furthermore, past researchers have shown that large particles are ineffective as toughening agents\textsuperscript{51}, and that crack growth may become more preferred at high volume fractions leading to decreased toughness\textsuperscript{50,62,63}.

Based on these findings, we finally made a series of samples with a variety of void sizes and concentrations, to see if voids would significantly toughen epoxies in a different range of sizes and concentrations. We then fractured the samples in a 3-point bend test. From this study, we found that in samples with a lower volume fraction of voids and significantly smaller voids, a whitened zone appeared in front of the crack tip and the samples became significantly tougher. The values of fracture toughness of these samples are not reported here, because the test measurements were not carried out in a rigorous manner. However from the micrographs of the fractured surfaces in Figure 6.10, we see
Figure 6.10: SEM micrographs of fracture surfaces from 3-point bend samples of propylbenzene-voided EPON 828 cured with AEP, that were fractured at either liquid nitrogen temperature or 20°C. a) 1.7% voids, cryofractured; b) 1.7% voids, fractured at 20°C; c) 6.4% voids, cryofractured; d) 6.4% voids, fractured at 20°C; e) 26% voids, cryofractured; f) 26% voids, fractured at 20°C.
that inelastic void growth is observed in the samples with smaller and fewer voids. As the volume fraction and size of the voids increased to 26%, the size of the whitened zone decreased and inelastic void growth becomes less noticeable (see Figure 6.10c). When the void content reached 32%, the materials were brittle with no stress whitening nor significant inelastic void growth observed. These final results confirm the previously published work of others\textsuperscript{39,49,49}, showing that the addition of microvoids to a matrix can significantly toughen the material. And that the reported energy absorbing mechanism of inelastic void growth is observed in the materials with smaller and fewer voids.

6.4 Conclusions Regarding Microvoided Epoxies

Microvoided epoxies have been made with a variety of void sizes and volume fractions. The goal of this work was to understand how the yield behavior and fracture toughness of glassy polymers are affected by the presence of microvoids. Compression tests on samples with void volume fractions ranging from 0 to 32% showed that the compressive yield strength of these materials decreases approximately linearly with increased void content. However, the decrease in yield strength with increase void content is slightly under-predicted by Lazzeri-Bucknall yield function. The fact that the measured yield strengths are below the model predictions suggest that other aspects not accounted for in the model (e.g., particle interactions, polydispersity in spacing, etc.) may be operative.

Hollow cylinders of these voided epoxies were tested in stress states ranging from uniaxial compression to biaxial tension. The results showed that the yield behavior of these microvoided materials followed a modified von Mises yield criterion, which is in contrast to
that predicted by a modified Gurson type model. However, in our studies no significant
inelastic void growth, the basis of the model, was observed in the biaxially loaded samples.
It is believed that the lack of inelastic void growth in the samples and the lack of
nonlinearity in the measured yield envelopes is due to the range of void sizes and
concentrations that were studies. It is also possible that the most biaxial stress state, biaxial
tension, is not confined enough for significant inelastic void growth to occur. However,
 improved techniques of measuring inelastic void growth are also needed.

The reason that we believe that this lack of inelastic void growth is related to the
range of void sizes and concentrations that were studies comes more from the fracture
toughness tests than from the hollow cylinder tests. This is because the fracture toughness
of these voided materials was found to increase and inelastic void growth was observed
only in the samples with the smallest and lowest volume fraction of voids. Therefore when
the voids are small and their concentration is low, we believe that voids could replace
rubber particles in toughened polymers. However when the voids' size and concentration
get too high, the viewpoint that voids embrittle glassy polymers appears to be correct. The
reason for this change in toughness with void concentration and size has yet to be
determined. Also note that the toughening mechanism of crack bridging by the rubber
particles does toughen glassy polymers in a manner that is not possible in the presence of
voids. However crack bridging was not considered in the above discussion.
BIBLIOGRAPHY


