Effect of Network Structure/Topology on Mechanical Properties of Crosslinked Polymers

A Thesis

Submitted to the Faculty of Drexel University by Majid Sharifi in partial fulfilment of the requirements for the degree of Doctor of Philosophy May 2015
Dedications

To my family, my wife and her family for their invaluable support and inspiration.
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Abstract

Effect of Network Structure/Topology on Mechanical Properties of Crosslinked Polymers

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The interest in epoxy thermosetting polymers is widespread (e.g. Boeing 787 Dreamliner, windmill blades, automobiles, coatings, adhesives, etc.), and a demand still exists for improving toughness of these materials without degrading advantageous properties such as strength, modulus, and $T_g$. This study introduces novel approaches for improving the intrinsic mechanical characteristics of these polymers.

The designed synthetic techniques focus on developing polymer materials with the same overall compositions but varying in network topologies, with distinct topological features in the size range of 5-50 nm, measured by SAXS and SEM.

It was found that without altering chemical structure, the network topology of a dense thermoset can be engineered such that, under mechanical deformation, nanocavities open and dissipate energy before rupturing covalent bonds, producing a tougher material without sacrificing strength, modulus, and even glass transition temperature. Modified structures also revealed higher resistance to fracture than the corresponding control structures. The major fracture mechanism responsible for the increased energy dissipation was found to be nano-cavitation. SEM images
from the fracture surfaces showed clear cavities on the modified samples whereas none were seen on the fracture surface of the control samples.

Overall, it was demonstrated that network topology can be used to tailor thermal and mechanical properties of thermosetting polymers. The experimental methodologies in this dissertation can directly and economically be applied to design polymeric materials with improved properties for desired applications. Although topology-based toughening was investigated on epoxy-amine polymers, the concept can be extended to most thermoset chemistries and perhaps to other brittle network forming materials.
Chapter 1. Introduction

Thermosetting materials are one important class of polymer materials that have been widely used for many years. These polymers form crosslinks between polymer chains during cure. Due to the inherent crosslinked nature of these polymer materials, they typically show relatively high thermal and mechanical stability, stiffness and strength compared to thermoplastic polymers. Therefore, they are better candidates for conditions where durable materials are desired, particularly at relatively higher temperature demands.

Epoxy resins are one of the most important and widely used thermosets. Epoxy composites are extensively used as the structural materials in aviation (Boeing 787 Dreamliner), and automobile manufacturing industries because of their high strength-to-weight ratio, relatively high modulus, and low processing and maintenance cost. In addition, epoxy resins are widely used in coating because they guarantee excellent adhesion and high chemical resistance. They are also used in electrical systems and electronics due to their low electrical and heat conductivity.

Despite their desirable properties, epoxy thermosets are inherently brittle in nature due to the densely crosslinked network structures that form upon curing.
cured, they exhibit poor resistance to fracture,\textsuperscript{2-5} so they generally break before yielding with relatively low energy absorption before failure.\textsuperscript{6}

Significant effort has been dedicated toward developing methods to toughen epoxy systems. Toughening of epoxy polymers has been achieved using: micro-sized liquid rubber,\textsuperscript{7} thermoplastic particles,\textsuperscript{8-10} core-shell rubber particles,\textsuperscript{11, 12} elastomers,\textsuperscript{13} diblock copolymers,\textsuperscript{14-16} and interpenetrating networks.\textsuperscript{17} Although these techniques achieved success in toughening thermosets, it has been widely observed that the presence of a soft second phase matter such as rubber particles, thermoplastic particles, or a low-stiffness interpenetrated network reduces the modulus, strength and, more importantly, glass transition temperature of the resulting system.

Recent molecular-simulation work uncovered a significant finding: Using coarse-grained molecular simulations of highly crosslinked polymer networks, Mukherji et al.\textsuperscript{18, 19} observed the opening of many small random voids upon uniaxial tension, leading to a significantly high energy absorption before break. The void opening mechanism upon uniaxial tension was not observed for the similar crosslinked polymer networks in which bonds were constrained such that void openings were restricted. The representative stress-strain curve of the two systems revealed that the observed toughening was achieved with no sacrifice in Young’s modulus and strength.
This major finding is the basis of the current dissertation. The principle focuses of this study are: (1) synthesis of amine-cured epoxy systems with the same overall composition but varying network topologies (also called “polymer network isomers”), with controlled topological features in the size range of 5-50 nm; (2) characterizing the topological variations using the existing nanoscope instrumentations; (3) material characterization to link polymer network topology to mechanical properties. The end results promote an understanding of the fundamental question: To what extent can network topology affect the mechanical properties of crosslinked polymers? The impact of this work will consist of developing a new generation of epoxy resins that are resistive to fracture and failure, and unlike other toughening conventions, will preserve the essential properties such as mechanical strength and stiffness and glass transition temperature.

In this study, there are three suggested approaches of synthesis through which polymer networks with the same overall compositions but vary in network topology are synthesized. Figure 1.1 schematically demonstrates the approaches that are considered in this study.
Figure 1.1. Topographical schematics of the polymer network isomers that will be considered in this work. (a) Reactive Encapsulation of Solvent (RES), (b) Diamine-functionalized Partially Reacted Substructures (dPRS), (c) Monoamine-functionalized Partially Reacted Substructures (mPRS).
Accordingly, Chapter 3 introduces a new strategy of developing epoxy-amine thermosetting polymers with altered topology using a non-reactive solvent during cure. The synthesis methodology used in this Chapter is termed “Reactive Encapsulation of Solvent (RES)”. This Chapter describes how the manipulation of network topology could induce remarkable plastic behavior to glassy networks subjected to high load environments. It was found that without altering chemical structure, the network topology of a dense thermoset can be engineered such that, under deformation, nanometer-sized cavities open and dissipate energy before rupturing covalent bonds, producing a tougher material without sacrificing tensile strength, modulus, density, or glass transition temperature.

Chapter 4 gives an overview of employing equilibrium swelling to investigate and characterize the network structure of crosslinked polymers that are formed/cured in dilute environments, i.e. in presence of excess inert solvent during cure. The findings of this study suggest that the traditional models don’t accurately represent swelling behavior of epoxy-amine gels prepared in highly dilute environments as they over-predict the molecular weight between crosslinks. A straightforward modification to existing models was adopted to correct for this, and additional insight was gained in understanding the changes in network topology that occur when inert solvents are used for the synthesis of epoxy-amine networks. Some of
the results presented in this Chapter are reproduced with permission from the works of Ghorpade\textsuperscript{20} and Raman.\textsuperscript{21}

Chapter 6 explains the effect of materials’ $T_g$ on behavioral characteristics. Accordingly, three different epoxy-amine thermosetting systems with $T_g$’s ranging from 60 °C – 180 °C were investigated. The findings in this Chapter provide additional insight in understanding the flexibility of the crosslinkers on the mechanical behavior of thermosets when network topology is altered.

Chapters 5 and 7 introduce a novel technique in developing the polymer network isomers using a solvent-free protocol. These Chapters reveal that the synthesis of epoxy-amine networks that have the same overall composition but vary in network topology, result in some of the network isomers having unprecedented concomitant gains in fracture toughness and $T_g$, without degrading strength and modulus. The presented molecular simulations results are reproduced with permission from the works of Jang and Abrams.\textsuperscript{22}

The end results demonstrated that network topology can be used to tailor the behavior of thermosetting materials without the incorporation of toughening agents that often reduce processing ease and are costly. The resins developed based on the addressed protocols can be used directly to formulate new epoxy-amine systems for coating, adhesive and composite applications. The concepts can also
be extended to most thermoset chemistries and perhaps also to other brittle
network forming materials.

1.1. List of References


Chapter 2. Background

2.1. Introduction

Thermosetting polymers are a type of polymeric materials that irreversibly cure. Cure can be carried out through heating, radiation, or chemical reactions. The cured polymers form a network structure, because of the presence of crosslinking between polymer chains. Because of the inherent crosslinked structures, they are strong and thus used in broad range of applications. Amine-cured epoxy systems which will be discussed in-depth in this dissertation, generally form via a series of chemical reactions between epoxide and amine groups as represented in Figure 2.1. The reason for choosing amine-cured epoxy thermosets for this study was due to the formation of the relatively homogenous polymer networks after cure, because the polymerization is known to be via “step-growth polymerization” for this polymers.
Figure 2.1. Scheme of epoxy-amine reactions. Step 1 is the epoxide-primary amine, and step 2 is the epoxide-secondary amine.
2.2. Step-Growth Polymerization

Step-growth polymerization refer to a type of reaction mechanism that monomers react to form dimers, trimers, then longer oligomers and eventually long chain polymers. If the functionality of the monomers are more than two, then crosslinking appear during the reactions. As polymerization proceeds, the polymer cluster grow until a percolation path is formed. This stage of polymerization is known as the gel point, where the steady shear viscosity suddenly jumps. After gelation, the reaction kinetics is diffusion controlled. Polymerization continues while crosslinking density increases. This step is known as vitrification. Glass transition temperature goes up until full conversion achieved. Figure 2.2 demonstrates a schematic representation at each stage of polymerization.
Figure 2.2. Schematic of a multifunctional monomer growth during step-growth polymerization. The red line is the percolated path at the gelation point.
2.3. Epoxy-Amine Reactions

The addition reaction of epoxide and amine is known to occur stepwise as shown in Figure 2.1. Step 1 represents an addition reaction between primary amines and epoxide functional groups, and step 2 indicates the addition reaction between secondary amines and epoxide groups. In some literatures, the reaction rate constant for both reactions assumed to be equal, however, in some others it is shown that they are not equal and their rate constant ratio $k_2/k_1$, also known as substitution factor, is a determining factor of the final network topology. Hydroxyl groups are also generated in step 1 and 2. They act as catalyst for the epoxy-amine reactions and affect the reaction rate constants, substitution factor, and consequently topological structure of the matrix. Homopolymerization reactions of epoxides are excluded since they are reported to occur only in the presence of the Lewis acid type catalysts. Etherification reactions are known to happen, however, experimental results show that this type of reactions is very improbable to occur or the amount of products are negligible compare to the amount produced in step 1 and 2 at stoichiometric mixtures of diepoxide and aliphatic diamines. Ochi et al. reported that less than 20% of epoxide groups consume in etherification reactions for a mixture of stoichiometric DGEBA-aliphatic diamines without the presence of an accelerator such as salicylic acid. Although, influence of etherification is reported to be larger when aromatic
diamines used as the curing agent. In this case, etherification reactions becomes more significant on account of low reactivity of secondary amine with respect to primary amine.\textsuperscript{14,15} After full conversion, a highly crosslinked structure obtained. Figure 2.3 is showing a crosslinked network structure for a stoichiometric blend of a typical epoxy (DGEBA) and a cycloaliphatic amine (PACM).
Figure 2.3. Molecular structure of a crosslinked polymer network.
2.4. Cure Kinetics and Network Structure

The physical properties and behavioral of epoxy-amine polymer networks during cure have been elucidated over the last two decades. Gillham et al.\textsuperscript{5,16} showed that curing reaction of epoxy-amine mixtures, e.g. Epon-828/PACM-20, is always accompanying with an initial devitrification, a vitrification, and a final devitrification point if epoxy/amine batch put under continuous heating at a constant rate. In their study, glass transition temperature has been determined at different stages of cure. They also showed that $T_g$ goes up as the curing reactions proceed. This increasing trend of glass transition temperature during cure is an indication of the formation of crosslinks for multifunctional monomers. As the degree of crosslinking increases, viscosity, the degree of rotational restrictions and the free volume fraction of the network are affected.\textsuperscript{17-19} According to Sanford and McCullough,\textsuperscript{17} glass transition temperature is a critical structural parameter that can reflect a measure of free volume available and the degree of rotational restrictions for polymer chain mobility.

Bueche et al.\textsuperscript{20} modeled the free volume fraction as a linear function of the difference of temperature from $T_g$. This relation is shown in the following equation.
\[ f = f_g + \alpha_f (T - T_g) \]  \hspace{1cm} (2.1)

In that, \( f_g \) is the fractional free volume at \( T = T_g \) and \( \alpha_f \) is the thermal expansion coefficient. Cohen and Turnbull\(^{21}\) reported the values of \( f_g \) and \( \alpha_f \) for an epoxy/amine system. In their works, \( f_g \) and \( \alpha_f \) determined to be 0.025 and \( 4.8 \times 10^{-4} \text{ °C}^{-1} \) respectively.\(^{21-23}\) Glass transition temperature at certain stages of cure can be evaluated from the well-known Dibenedetto equation.\(^{24}\)

\[ \frac{T_g - T_g^o}{T_g^o} = \frac{(\frac{E_x}{E_m} - \frac{F_x}{F_m})X}{1 - (1 - \frac{F_x}{F_m})X} \]  \hspace{1cm} (2.2)

This equation relates glass transition temperature to lattice energies and segmental mobility of crosslinked and uncrosslinked polymers. In that, \( \frac{E_x}{E_m} \) represents the ratio of lattice energies for crosslinked and uncrosslinked and \( \frac{F_x}{F_m} \) is the corresponding ratio for segmental mobilities. \( T_g^o \) and \( X \) are the glass transition temperature for uncured reactants and the fractional conversion for the epoxy-amine reaction respectively. For a system of Epon-828/PACM-20 the values of \( \frac{T_g^o}{E_m} \) and \( \frac{F_x}{F_m} \) are given as -19 °, 0.34 and 0.19 respectively.\(^{5}\) According to Dibenedetto equation, addition of a rubber or a plasticizing agent can lower the value of \( T_g \) through increasing the segmental mobilities of crosslinked and uncrosslinked polymers.
2.5. Time-Temperature Superposition (TTS)

The time-temperature superposition principle states that for a viscoelastic material that has molecular structure, time is equivalent to temperature, or temperature is a measure of molecular motion. In other words, at elevated temperatures times move faster for the molecules. According to the TTS principle, time and temperature are identical to the extent that data at one temperature can be superimposed on data at another temperature by shifting the curves along the log (time) axis.\(^{25}\) The activation energy required for a system to pass a transition state can be measured by the Arrhenius equation as following:

\[
\log a_T = \frac{E_a}{R} \left( \frac{1}{T} - \frac{1}{T_r} \right) \tag{2.3}
\]

where \(a_T\) is the shift factor, \(E_a\) is the activation energy for the transition, \(R\) is the universal gas constant, and \(T_r\) is the reference temperature.

Accordingly, the Williams-Landel-Ferry (WLF) equation expresses the relationship between time and temperature.\(^{26}\)

\[
\log a_T = \frac{-c_1 (T - T_0)}{c_2 + (T - T_0)} \tag{2.4}
\]
Where $C_1$ and $C_2$ are the WLF constants, $T_0$ is the reference temperature and for most polymers $T_g$ is taken as the reference temperature and $\alpha_T$ is the shift factor.

2.6. Modification to Polymer Network Structure

In fact, the brittleness of epoxy networks is primarily due to the degree of crosslinking density.$^{27}$ Significant amount of works dedicated to modify the network structure of epoxy systems. In early studies, introducing a secondary phase component, mainly a plasticizer to a network,$^{28-31}$ was proposed as an effective way to improve long strain properties such as toughness. However, resultant toughened networks always had lower $T_g$ and modulus.

Bennet and Ferris$^{28}$ improved the toughness for a system of epoxy/amine through incorporation of reactive amine-terminated oligomers. They showed that when the amine-terminated oligomers are applied at a sufficient level to form a material consisting of a lightly crosslinked thermoplastic continuous within epoxy/amine phase, the fracture energy increases accompanying with almost zero or slight increase in modulus. Moreover, the effect of linear chain fraction on mechanical properties of highly crosslinked polymer networks has been shown through the use of molecular dynamic simulation.$^{32}$ In that work, within increasing the linear chain
fraction of oligomers, the ductility (strain-to-failure) decreases until a threshold value beyond which the ductility increases with increasing of linear chain fraction of oligomers.

More recently, investigations are primarily focused on addition of nanoparticles to obtain a toughened epoxy. Although diluents usually degrade $T_g$ and modulus, application of nanoparticles could result in getting a toughened network with minimal impact on glass transition temperature and modulus. In a separate study, Pearson et al. showed that toughening mechanisms are particle-dependent. In fact, relatively large particles observe to provide a modest increase in fracture toughness; however, small particles provide a remarkably large increase in toughness through cavitation-induced shear bonding mechanism.

Raman in a separate work suggested a way through which one can modify and change a thermosetting network molecular architecture and subsequently manipulate mechanical and transport properties of the resultant matrix. It is proposed that epoxy addition to a primary amine could affect the reactivity of the secondary amine and might change the basicity of amino group. It is hypothesized that it can affect the network topology and structural properties thereafter. The parameter, $k_2/k_1$, is a key parameter for predicting the structure of the resulting network, which itself can be influenced by reaction rate parameters such as cure
temperature. Evidences show that a diffusion limitation always affects the final stages of cure. Sourour and Kamal\textsuperscript{41} and Wisanrakkit and Gillham\textsuperscript{5} showed that an intrinsic third-order autocatalytic reaction can best model the cure of epoxy-amine polymerization. However, the model is incapable of predicting the reaction once the reaction extents to certain degrees of polymerization. Some literatures show that the reaction cannot assume to be kinetically controlled once it reaches to the extents corresponding to vitrification points.\textsuperscript{5, 22, 23, 42, 43} In other words, as the reaction proceeds to the point where the fractional conversion represents the point of vitrification, the network no longer stays in its rubbery phase and it suddenly jumps to glassy state region in Time-Temperature-Transformation, TTT diagram.\textsuperscript{5, 16} In the glassy state, the reactants must diffuse through the network so that they collide and make the reaction to occur. Therefore at relatively high conversion, we should expect a deviation from the third-order autocatalytic intrinsic model. Experimental results demonstrated this deviation.\textsuperscript{5, 22, 23} Klein et al.\textsuperscript{42, 43} used Rabinowitch equation\textsuperscript{44} as a relation for global reaction rate constant of epoxy-amine polymerization in terms of diffusive and chemical parameters. They related diffusivity of amine reagents within epoxy to the number-averaged molecular weight of the network, $M_n$. And from Marten and Hamielec equation,\textsuperscript{45} they obtained a global rate constant as a function of number-averaged molecular weight through which they could predict the kinetics of the cure reaction at almost every stages of polymerization. The diffusion limitations discussed so far could
potentially influence the topological structure of the final network by decreasing the reaction rate, limiting the conversion and disrupting the network connectivity.  

2.7. Structure-Related Properties

The correlations for physical and mechanical properties of epoxy/amine thermosets have been widely investigated. The structural variation for correlation studies mostly introduced through stoichiometry, cure cycle, reaction conversion and prepolymer with different molecular weights. Polymer networks mostly characterized by measuring crosslinking density, average molecular weight between crosslinks, free volume fraction, specific volume or bulk density as a measure of molecular packing, and glass transition temperature. Density and molecular packing, or free volume fraction, can be considered as the main factors which can affect small-strain properties such as room temperature modulus and yield strength. Several studies investigated the influence of cure temperature, and reactant composition on glassy modulus. They showed that modulus decreases with increasing cure temperature. Similarly, yield strength in glassy state is primarily depending on free volume and hence it decreases as a result of free volume increase. On the other hand, tensile strength and failure strain as the large-strain properties usually
exhibits a complex dependence on structural properties. In relating tensile strength to crosslink density varied by changing the ratio of hardener to resins, researchers found either a growth,\textsuperscript{55} or degradation,\textsuperscript{52} in strength level. In contrast, some others reported no significant interdependence.\textsuperscript{56} Similar inconsistency has been found for failure strain when people tried to elucidate the effect of stoichiometry.\textsuperscript{51, 52, 56, 57} The reason might be owing to the fact that changing crosslinking density through varying stoichiometry could also change the network topology, and thus varying the stoichiometric ratio of resin to hardener is not an effective way to characterize network structure attributed solely to crosslinking density or free volume fraction.

2.8. List of References


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Chapter 3. Epoxy Thermosets with Altered Network Topology via Reactive Encapsulation of Solvent; Synthesis and Characterization

3.1. Introduction

As discussed, epoxy materials are extensively used because they typically guarantee excellent adhesion, high chemical and heat resistance, good-to-excellent mechanical properties, and relatively good electrical insulating properties. Many attempts have been made to improve their resistance to abrasion when used as coating materials. Structural epoxy-based composite materials are becoming prominent in a vast number of applications where a material with relatively high strength, high modulus and light-weight is needed. It is well known that epoxy thermosets are brittle due to their highly crosslinked networks, and exhibit poor resistance to fracture. These polymer materials generally break before yielding without plastic deformation with relatively poor energy absorption before failure.

Conventional toughening methods, for example, micro-sized liquid rubber, thermoplastic particles, core-shell rubber particles, elastomers, diblock copolymers, and interpenetrating networks were successful at toughening thermosets, however, it is widely observed that the presence of a soft second phase
matter such as rubber particles, thermoplastic particles, or a low-stiffness interpenetrated network reduces the modulus, strength and, more importantly, glass transition temperature of the resulting system. Developing methods to toughen epoxies without sacrificing these advantageous properties remains paramount.

Recent molecular-simulation work points to a possible solution: Using coarse-grained molecular simulations of highly crosslinked polymer networks, Mukherji et al.\textsuperscript{8,9} observed the opening of many small random voids upon uniaxial tension, leading to a clear strain-hardening regime. These voids were not present in the unstressed samples but were encoded by the non-uniform directionality of the crosslink bonds, and these authors further showed that by tetrahedrally distributing crosslinks emanating from each particle, these voids could be suppressed, generating samples of the same density and ultimate strength as the more random samples. This work suggests that altering the network connectivity of a crosslinked polymer without changing the crosslink density offers a route to increasing toughness without sacrificing strength.

Previous experimental work in our group offers a possible route toward realizing this suggestion. Raman et al.\textsuperscript{21,22} proposed a method through which a polymer network could be tailored via a miscible and chemically inert solvent present
during cure. The technique was termed Reactive Encapsulation of Solvent (RES). This method involves the synthesis an epoxy thermoset in presence of an inert solvent without microphase separation. It was shown that when the step-growth polymerization reactions take place in presence of an inert solvent that is miscible with the monomers and resulting polymer, the polymer network encapsulates the solvent species without covalent bonds being formed in the regions where inert solvent species are present. Consequently, a nanoporous polymer network is obtained upon solvent removal using supercritical extraction and drying.\textsuperscript{21,22} If, as is done in this work, solvent removal is conducted simply by heating the organogels following network formation, the pores collapse leading to samples with the same density as non-RES-modified epoxies. This method of network synthesis is termed as Reactive Encapsulation of Solvent-Drying (RESD) approach.

The purpose of this article is to demonstrate how RESD can indeed generate toughened epoxy materials without sacrificing density, strength, or glass-transition temperature, for a particular epoxy/crosslinker/solvent system. All-atom molecular dynamics simulations of the same systems further illustrate that RESD yields inter-crosslink contour-length distributions shifted to higher values, indicating that indeed network topology is predictably influenced by RESD.
3.2. Experimental

3.2.1. Materials

The materials used in this study are shown in Figure 3.1. The difunctional epoxy resin used is Diglycidel Ether of Bisphenol-A (DGEBA), EPON 828 with $n=0.13$, (Miller-Stephensen Chemical Co.). The curing agent is an aliphatic tetrafunctional diamine, polyetheramine (Jeffamine D-400) with an averaged molecular weight of about 430 g/mol (Huntsman). Dichloromethane (DCM) (Sigma-Aldrich) was used as the inert solvent for the RESD technique.
Figure 3.1. Molecular structures of (a) Diglycidyl Ether of Bisphenol-A (DGEBA), EPON 828, n=0.13, (b) Polyetheramine (Jeffamine D400), x=6.1, (c) Dichloromethane (DCM).
3.2.2. Solvent Selection

According to Raman et al.\textsuperscript{22}, the solvent used in RES has to be miscible in DGEBA and Jeffamine D400 for the entire polymerization. It also must not phase separate before or during cure. Additionally, it is essential that the solvent species remain inert during polymerization reactions and not react with any of the reactive moieties at the curing temperature. The solvent molecules should also have a low boiling point and optimal favorable interactions with polymer chains so that they can be easily removed after polymerization but are soluble in the polymer. It is also preferred that the solvent has a low vapor pressure to minimize solvent loss during polymerization reactions at elevated temperatures. Taking into account all the above, DCM was selected as the solvent. Fourier Transform Infrared Spectroscopy in near infrared region revealed the inertness of DCM during the epoxy-amine reactions at the temperature of interest. The good miscibility observed for DCM in the reacting system likely stems from favorable weak dipole-dipole interactions involving hydroxyls formed during the ring opening reaction of DGEBA. Sample transparency (refractive indices of 1.5-1.57 and 1.42 for epoxy and DCM, respectively) before and after cure indicated the miscibility of dichloromethane during epoxy-amine reactions without macro/micro phase separation. Provided
the criteria for selecting a solvent described above are met other solvents can be used to create networks of altered topology.

3.2.3. Resin Selection

Solvent species typically exhibit poor diffusion rate through highly crosslinked membranes.\textsuperscript{23, 24} Additionally, in a numerical study Rohr and Klein proposed that diffusivity of chemical species is strongly influenced by species chain lengths.\textsuperscript{25, 26} The preliminary experiments conducted with the epoxy resin EPON 828 and crosslinker 1,4-bis(aminocyclohexyl)methane (PACM-20). Thermogravimetric results showed that the diffusion rate of DCM through a membrane made from an aromatic epoxy resin such as DGEBA and an aliphatic amine hardener like Jeffamine D400 is about 3 to 4 times greater when compared to a system composed of same epoxy resin cured with a cycloaliphatic amine such as PACM. It is believed that the higher diffusivity of DCM in the Jeffamine-based epoxies is attributed to the greater segmental flexibility of Jeffamine (and the lower T\textsubscript{g}). So, although polyetheramine as the curing agent provides a relatively low glass transition temperature, it was used as the curing agent in this study since it eases the solvent removal step.
3.2.4. Resin Processing

The sample batches were named by the weight ratio, labelled “DEA”, of DCM to the epoxy-amine resin used. For example, a “DEA 1” labelled sample has an equal weight of solvent to epoxy-amine monomers and so it is 50% solvent by weight. Batches with DEA’s of 0, 0.5, 0.75, 1, and 1.5 were prepared. EPON 828 resin was put in vacuum prior to mixing to remove water and other impurities. The purity of the EPON resin was confirmed using GPC. The value of epoxy equivalent weight, EEW, for EPON 828 was taken as 185-192 gr/eq from the material spec sheet. Jeffamine D-400 was used as received, and the amine hydrogen equivalent weight, AHEW, was assumed to be 115 gr/eq according to the material data sheet. Epoxy and amine were mixed in 2:1 molar ratio assuming ideal case where each tetrafunctional amine reacts with two difunctional epoxies. Samples were mixed in a centrifugal mixer at 2000 RPM for 10 min to ensure good mixing. The mixing process continued until a clear transparent liquid was obtained. The samples were then poured in a perfectly sealed container to minimize loss of DCM during cure. PTFE tubes with tube vacuum couplings provided the sealed environment.
3.2.5. Curing Procedure

One challenge was to find the optimum curing temperature at which the polymerization approaches adequate conversion while at the same time guaranteeing the container could sustain the pressure produced by the DCM. Previous studies confirm that the rate of epoxy-amine reactions is lowered in the presence of inert solvent due to reactant dilution. Preliminary kinetic results showed that curing reactions become extremely slow at temperatures below 50°C in the presence of DCM. DCM has a vapor pressure of approximately 2000 mmHg at 70°C, presenting experimental challenges with sealing the curing vessel for curing temperatures above 70°C. We therefore were limited to a maximum curing temperature of 70°C. All samples were kept at the reaction temperature for a total of three days to ensure the concentration of unreacted moieties is approximately zero (measured using Fourier transform infrared spectroscopy, detailed below). The same curing protocol was used for all batches including 0 DEA. All samples were weighed before and after cure to verify no solvent/resin was lost during cure. It was observed that the relative volume shrinkage after drying was larger for the specimens with higher initial solvent content.
3.2.6. Fourier Transform Infrared Spectroscopy (FTIR)

In order to monitor the epoxy-amine reactions and to investigate the inertness of solvent molecules during epoxy-amine reactions, FTIR in the near-infrared region (4000-8000 cm\(^{-1}\)) was used. A NIR spectrometer Nexus 670/870 (Thermo Nicolet Corp.) with CaF\(_2\) beam splitter was employed for this purpose. Capillary glass tubes (ID = 1.6 \pm 0.05 mm) were used to hold the samples. The tubes were sealed to ensure no solvent leakage during data acquisition. NIR spectra were collected at a resolution of 4 cm\(^{-1}\) in absorbance mode. The near infrared region was chosen since all the reactive moieties can be monitored. The peaks involved are the epoxy peak at 4530 cm\(^{-1}\), the primary amine peak at 4925 cm\(^{-1}\), and the primary/secondary amine peak at 6510 cm\(^{-1}\).\(^{30}\)

3.2.7. Thermal Drying

All samples were oven-dried at 120\(^\circ\)C for about 20 days. The weight of each sample was recorded at regular time intervals. After 20 days, the oven was turned off and with the door closed, the samples were gradually cooled to room temperature. The time between cooling and mechanical testing was approximately the same for all samples, minimizing differences resulting from physical aging below \(T_g\).
3.2.8. Dynamical Mechanical Analysis (DMA)

A TA instrument Q800 DMA apparatus was utilized to measure the viscoelastic properties and $T_g$. All specimens were tested at a constant frequency of 1 Hz. The oscillation amplitude was kept at 15 $\mu$m in single-cantilever mode. All samples were sanded into rectangular slab geometry (35-36 mm in length, 10-12 mm in width and approximately 2 mm in thickness). Test was conducted with a scanning rate of 1°C/min starting from room temperature to 140°C to obtain sufficient data below and above the glass transition temperature. The $T_g$ value was taken from the position of the peak of the loss modulus curve.

3.2.9. Density Measurement

The specific gravity and density of the resulting polymers was measured through the water displacement technique as described in ASTM D792. All specimens were well-polished and immersed in DI water at room temperature i.e. 23 °C. A setup as described in ASTM D792 was used to measure wet weights and density was measured using the procedures described therein.

Density values at the elevated temperatures (e.g. $T = T_g + 40$) were found by adjusting the room temperature density using volume expansion data obtained using a TA Instruments Q400 TMA apparatus.
3.2.10. Quasi-static mechanical properties

Uniaxial quasi-static mechanical properties in tensile and compressive modes were determined using a servohydraulic INSTRON apparatus model 8872. Five identical specimens were prepared for each sample type. They were cut into a rectangular slab geometry and then plastic tabs glued at each end. They were also well-polished to minimize the adverse effect of surface roughness on the resulting stress-strain curves. All dimensions were uniform with a standard deviation of ±1%. All samples were drawn under a uniaxial tensile loading rate of 0.5 mm/min at room temperature. The compression specimens were prepared the same way where five identical cubic specimens (3x3x3 mm ± 2%) were put in order for each of the sample types. Compressive load was applied in the axial direction at a crosshead speed of 1 mm/min at room temperature. The stress-strain data was collected until the point of rupture.

3.2.11. Scanning Electron Microscopy (SEM)

High resolution micrographs were taken with a Zeiss Supra 50VP equipped with an in-lens imaging detector. The samples were all broken at either room temperature or in liquid nitrogen. All the fractured surfaces were platinum sputtered for 25 seconds prior to imaging. The sputtering duration is selected to
avoid covering the visible features on the broken surfaces with the sputtering material.

3.2.12. All-atom Molecular Dynamics (MD) Simulations

The GAFF force field,\textsuperscript{31, 32} and the LAMMPS simulation package,\textsuperscript{33} was used to conduct all-atom MD simulations of stoichiometric Epon/Jeffamine/DCM epoxies. Each simulation system was generated by first placing stoichiometric amounts of Epon828 and Jeffamine-D400 (J400) were followed by the desired amount of dichloromethane to obtain low density mixture in a periodic box. The concentration of DCM in the mixtures was identical to those the experiments; i.e., 0%, 33%, 40%, and 50% by weight DCM. Four replicas per DCM concentration were generated. A series of NVE (constant number, volume and energy) and NPT (constant number of atoms, constant pressure, and constant temperature) simulations were initially performed on each system to achieve an equilibrium density value of about 1.07 g/cm\textsuperscript{3}. Then, a multi-step crosslinking algorithm was applied to make three-dimensional network structures.\textsuperscript{34} Polymerization involves the epoxide groups in Epon828 and the amine groups in Jeffamine D400 and results in a crosslinked network. Once a fully reacted crosslinked polymer was successfully achieved, DCM molecules were eliminated. Each system was annealed afterwards in the NPT ensemble for 5 ns at 600 K. Finally, each system
was cooled with a rate of 0.2 K/ps and equilibrated for 200 ps every 50 K decrement until 300 K was reached. Dijkstra’s algorithm was used to find minimum contour path length for each unique pair of amine nitrogen atoms. More details of the simulations are given in recently published work by our groups.

3.3. Results and discussion

3.3.1. Curing

Figure 3.2 shows FTIR spectra at various time-points over two days of curing at 70 °C for a typical DCM – DGEBA/Jeffamine D400 systems (0.5 DEA). These data indicate completion of epoxy-amine reactions in the presence of dichloromethane for stoichiometric amounts of DGEBA to Jeffamine D400 as the epoxy, primary amine, and primary/secondary amine peaks at 4530 cm⁻¹, 4925 cm⁻¹ and 6510 cm⁻¹ all disappear following cure.
**Figure 3.2.** FT-NIR spectra for epoxy-amine reactions for a sample containing dichloromethane (0.5 DEA) at 70°C.
3.3.2. Drying

Thermo-gravimetric data during post-cure drying are shown in Figure 3.3. The plateau in weight-vs-time indicates the termination of drying. In addition, weight loss was in good agreement with the initial amount of solvent used. Nearly 99% of initial solvent was removed in all cases.
Figure 3.3. Thermo-gravimetric analysis at 120 °C for samples with different initial solvent amounts.
3.3.3. Bulk Density

The original RES method using supercritical extraction was developed to synthesize nanoporous thermosets. In the RESD approach, drying above $T_g$ and long-time annealing is hypothesized to fully collapse these voids, yielding samples with the same density as neat-cured epoxies. Average density values and their standard deviations for the dried specimens at room temperature, and their corresponding estimated values for $T = T_g + 40 ^\circ C$ are listed in Table 3.1. Statistically invariant density values for all samples support the claim that the free volume fraction is comparable for unmodified and modified systems implying that the modified structures should have collapsed voids. Furthermore, equal density values at $T = T_g + 40 ^\circ C$ indicate that the hypothesized void structures remain collapsed in the rubbery state.
<table>
<thead>
<tr>
<th></th>
<th>( \rho ) at ( T=23^\circ C ) (g/cm(^3))</th>
<th>( \rho ) at ( T=T_g+40 ) (g/cm(^3))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 DEA</td>
<td>1.123 ± 0.002</td>
<td>1.106</td>
</tr>
<tr>
<td>0.5 DEA</td>
<td>1.127 ± 0.012</td>
<td>1.109</td>
</tr>
<tr>
<td>0.75 DEA</td>
<td>1.129 ± 0.005</td>
<td>1.112</td>
</tr>
<tr>
<td>1 DEA</td>
<td>1.129 ± 0.009</td>
<td>1.111</td>
</tr>
<tr>
<td>1.5 DEA</td>
<td>1.126 ± 0.012</td>
<td>1.109</td>
</tr>
</tbody>
</table>

**Table 3.1.** Averaged density values at room temperature and 40 °C above \( T_g \).
3.3.4. Dynamical Mechanical Properties

The hypothesis of polymer network structural differences for the resulting thermosets are investigated using dynamic mechanical analysis in this section. According to Raman et al.\textsuperscript{28} nonbonded domains form throughout a polymer network during step-growth polymerization in the presence of an inert solvent, leaving pores when the solvent is removed by supercritical extraction. However, thermal drying above \( T_g \) allows the polymer chains to relax and the resulting voids to collapse. The collapsed voids, referred to as “protovoids” in this study, do not provide additional free volume (as shown in the “Bulk Density” section). The concept is illustrated schematically in Figure 3.4 – note that in all cases each crosslinking point has the same number of connections and that after drying the density of the modified system is the same as that of the unmodified system. Therefore the glassy modulus of the modified thermosets is expected to be comparable to the value of the unmodified thermosets. DMA results described below indicate that the glassy modulus at room temperature for modified thermosets is comparable to that of the unmodified 0 DEA resin, implying that the probable structural variations do not sacrifice the material’s glassy modulus.
Figure 3.4. 2D schematic network structure of a neat-cured epoxy and modified epoxy through RES and RESD. The upper right is when solvent is removed through supercritical extraction and lower right is when solvent removed through thermal drying.
Figures 3.5 and 3.6 show the storage and loss moduli vs. temperature for the dried specimens. Additionally, Table 3.2 contains a summary for all samples tested of RT glassy modulus, rubbery modulus \((T = T_g + 40 ^\circ C)\), \(T_g\) obtained as the peak position of the loss modulus vs. temperature plots in Figure 3.7, and the height of the tan \(\delta\) peak. Based on the results shown in Table 3.2, the glass transition temperature has not been affected through the use of RESD. Considering the fact that solvent typically reduces the glass transition temperature as well as Young’s modulus, invariant \(T_g\) in our samples indicate that any residual solvent in the dried samples is negligible.
Figure 3.5. Dynamic Mechanical properties of the thermal heated samples with different initial solvent content. Storage Modulus vs. Temperature.
Figure 3.6. Dynamic Mechanical properties of the thermal heated samples with different initial solvent content. Loss Modulus vs. Temperature.
Table 3.2. DMA results: RT glassy modulus, rubbery modulus ($T = T_g + 40 \, ^\circ C$), glass transition temperature, and peak values of tan $\delta$.

<table>
<thead>
<tr>
<th></th>
<th>Glassy modulus (GPa)</th>
<th>Rubbery modulus (MPa)</th>
<th>$T_g$ ($^\circ C$)</th>
<th>Tan $\delta$ peak</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 DEA</td>
<td>2.30</td>
<td>10.71</td>
<td>59.9 ± 0.3</td>
<td>1.23</td>
</tr>
<tr>
<td>0.5 DEA</td>
<td>2.16</td>
<td>7.15</td>
<td>57.7 ± 0.9</td>
<td>1.45</td>
</tr>
<tr>
<td>0.75 DEA</td>
<td>2.35</td>
<td>5.92</td>
<td>59.2 ± 1.3</td>
<td>1.4</td>
</tr>
<tr>
<td>1 DEA</td>
<td>2.25</td>
<td>5.36</td>
<td>59.0 ± 1.1</td>
<td>1.55</td>
</tr>
<tr>
<td>1.5 DEA</td>
<td>2.25</td>
<td>5.21</td>
<td>58.5 ± 1.0</td>
<td>1.56</td>
</tr>
</tbody>
</table>
Although the glassy moduli and $T_g$ values are comparable for the dried unmodified and modified samples, the differences in tan δ peak and rubbery modulus were significant. The difference in tan δ peak is shown in Figure 3.7, and the variation of rubbery modulus will be elucidated in the next section.

The results indicate that both tan δ peak value and the area under tan δ is greater for modified samples. The tangent of the phase angle δ, tan δ, is defined as the ratio of loss modulus over storage modulus, which is a measure of energy dissipation. It also shows the extent of internal friction or damping and so this quantity is a sensitive measure of molecular structure in a polymer network. For two homogenous thermosets where the distribution of molecular weight between crosslinkable sites is almost uniform, the one with a loosely crosslinked network typically shows a higher peak value and subsequently a larger area under tan δ because viscous behavior dominates over elastic behavior, particularly above $T_g$. A highly crosslinked polymer network has a reduced chain slippage, and so a lower tan δ peak value at elevated temperatures. In the current study, it is shown that the peak values of tan δ are higher for the modified samples. It implies that either the crosslinking density is lower or relative chain slippage between crosslinks is higher for the modified samples, and thus the modified thermosets can absorb more energy under cyclic stress. Since both modified and unmodified thermosets are fully cured with the same density, and therefore must have
comparable crosslink densities, the observed difference in viscoelastic properties could be due to network topology differences.
Figure 3.7. Tan δ vs. temperature for unmodified (0 DEA) and modified (1 DEA) samples.
3.3.5. Topological Differences

One important observation in this study is the decreasing trend in rubbery modulus when increasing the initial solvent-to-monomer weight ratio of the dried samples (Figure 3.5).

The molecular weight between crosslinks, $M_c$, and crosslink density, $\nu$, for an amorphous polymer network above its glass transition temperature can be obtained using the following relations derived from rubber elasticity theory:\textsuperscript{39}

\begin{equation}
M_c = 3\frac{\rho RT}{E}\tag{3.1}
\end{equation}

\begin{equation}
\nu = \frac{\rho}{M_c}\tag{3.2}
\end{equation}

Crosslink density ($\nu$) and molecular weight between crosslinks ($M_c$), are plotted in Figure 3.8 as a function of initial solvent-to-monomer ratio using Equations 3.1 and 3.2 and density and rubbery modulus data obtained at $T = T_g + 40 \degree C$ given in Tables 3.1 and 3.2 respectively.
Figure 3.8. Apparent molecular weight between crosslinks and apparent crosslinking density vs. initial solvent-to-monomer weight ratio. Samples are fully reacted and identical in composition.
The reduced plateau rubbery modulus for modified specimens is not due to inadequate polymerization. NearIR spectra showed that epoxy-amine reactions are the predominant reactions for systems with or without solvent. Additionally, all show an ultimate conversion greater than 99% for epoxide reactive groups. Macosko et al.\textsuperscript{40} related the molecular weight between crosslinkable sites to the extent of crosslink formations. According to this theoretical relationship, the extent of reaction beyond gelation for the resulting thermosets should be much lower than unity to provide identical $M_c$ values corresponding to the ones measured for our modified samples. This difference is larger than the error attributed to the conversion levels obtained from NearIR and so the extent of cure is not the reason for the elevated values of molecular weight between crosslinks. Moreover, it has been discussed that glass transition temperature is a sensitive measure of extent of polymerization\textsuperscript{41-43} and any deviation from full cure conversion should result in a drastic decrease in the glass transition temperature. From this perspective, the comparable $T_g$ values indicate that the reduced rubbery plateau was not caused by differences in extent of polymerization.

The topological distance between crosslinks is anticipated to be a parameter that differs substantially when comparing unmodified to modified systems. This offers an explanation for the observed differences in rubbery plateau moduli that is not predicted by theory if the crosslink density is kept constant. Topological distance
is defined as the average of all distances from one crosslink point to all of the neighboring crosslinks when tracing the network, in contrast to spatial distance which is the average of all the straight distances from one crosslink point to all the neighboring crosslinks. The distinction between spatial and topological distance is shown in Figure 3.9. Note that for our dried systems the spatial distance between crosslinks does not vary because the number of crosslinks (composition) remains the same.
Figure 3.9. 2D schematic of an unmodified (left) and a modified (right) polymer network. Green lines are the topological distances, red arrows are the spatial distances and dots are crosslink points. Modified network structure has collapsed voids with identical intermolecular packing to the unmodified structure.
Considering an unmodified system, it is believed that the average topological distance from one crosslink point to all the neighboring crosslinks is comparable (although larger) to the average spatial distance. However, for a modified system, average topological distance is greater than the corresponding spatial distance. This concept is also illustrated in Figure 3.9. From statistical thermodynamics, the number of chain conformations and subsequently entropy will be higher for the modified systems assuming that the entropic term is governed by topological distance rather than end-to-end distance. Since retractive force and subsequently retractive stress of a polymer network in rubbery state is inversely proportional to the entropy of the system, the resulting rubbery modulus is reduced for modified systems. This could lead to observed apparent elevated molecular weight between crosslinks for the modified systems.

3.3.6. Swelling

Results of swelling experiments confirm that significant topological differences are introduced by curing the epoxy-amine systems in the presence of an inert solvent. Dried samples were soaked in dichloromethane at room temperature for a period of time sufficient to attain equilibrium. The observed equilibrium solvent mass uptake for the 0 DEA, 0.5 DEA, and 0.75 DEA samples was 111%, 150%, and 170% respectively. Thus equilibrium swelling increases with increasing solvent content.
used to prepare the samples. Since all the thermosetting systems are fully crosslinked, and chemically the same, the equilibrium mass uptake enhancement is a result of altered polymer network topology.

3.3.7. Minimum Topological Contour Lengths from All-Atom Simulations

So far, the hypothesis was that, presence of DCM should alter the topology of a crosslinked polymer network, since DCM molecules must restrict local directions in which crosslink bonds can form. It was also hypothesized that the topological distance is distinguishable between the two network structures. In order to investigate this question, the minimum contour path from every nitrogen atom to every other for each simulated crosslinked sample was measured using all-atom MD simulations. The average minimum inter-nitrogen contour path for each system is shown in Figure 3.10. Here a clear signature of the effect of including DCM during cure is observed, in that the minimum contour path distributions shift to larger path lengths as the during-cure DCM concentration increases. The effect is strongly pronounced at the largest path lengths. The results of a more detailed study by our groups have recently been published.36
Figure 3.10. Average minimum inter-nitrogen contour length as function of the initial amount of DCM from all-atom MD simulations.\textsuperscript{36}
The trend in minimum contour length with solvent content mimics that of the tan δ peaks and apparent molecular weight between crosslinks. Clearly the all-atom structures reflect the influence of solvent on the network topologies. This result is significant because the minimum contour path between any two points represents the largest Euclidean distance to which those points can be separated in straining the system before covalent bonds must yield. Therefore it is hypothesized that minimum contour paths between points in a network could influence large-scale material properties, such as toughness, that depend less on intermolecular packing and more on sacrificing covalent bonds. That we see twin correlations (a) between RESD solvent content and toughness and (b) between RESD solvent content and longer minimum contour paths justifies ongoing work in our labs to establish links between network topology and material properties.

3.3.8. Quasi-Static Tensile Properties

As shown, RESD does not sacrifice the glass transition temperature and glassy modulus of the cured thermosets. It was also discussed that the modified samples contain structural features in the form of collapsed voids. According to Mukherji et al.,\textsuperscript{8} expansion and growth of these protovoids without bond breaking is the microscopic origin of strain hardening in a glassy polymer which yields a more
ductile material. To investigate this hypothesis, mechanical response of each of the materials to uniaxial tensile and compressive loading was captured.

Uniaxial stress-strain curves for the unmodified and modified tensile coupons were recorded for at least five identical specimens for each data point. A very large plastic deformation for the modified samples was observed, as shown in Figure 3.11. Although necking starts for both types of specimens at strain values of around 10%, modified samples also exhibited extensive drawing. The drawing is a result of the local stress rising sufficiently during necking so that it is sufficient to stretch material at the edge of the neck increasing the size of the necked region. It is interesting to note that the behavior exhibited by the 1.5 DEA sample in Figure 3.11 is similar to that observed for semicrystalline thermoplastics where the ability to sustain drawing is a result of large changes in microstructure with significant strain hardening. Note that engineering stress and strain was used in reporting these data as this is the most common way of reporting such data. Furthermore, simple conversion to real stress strain does not provide additional insight since the necking results in an inhomogeneous distribution of strains and stresses along the length of the sample. Nevertheless it is important to realize that the stress in the necked region is significantly higher than shown by the stress-strain plots in Figure 3.11.
Figure 3.11. Engineering stress-strain curve for unmodified, 0 DEA, (solid black line) and modified, 1.5 DEA, (red dashed-line) samples in tensile mode.
Figure 3.12. RT-fracture surface of unmodified (a) and modified (b) structures. Scale bars are 1 µm in size. The schematic is representative of network deformations and bond reorientations during protovoid growth under tensile stress.
It is suggested that this remarkable improvement in ductility, or toughness, is primarily due to the topological differences between unmodified and modified polymer networks as discussed. Opening of protovoids without bond breaking would enable the thermoset to plastically elongate under tensile deformations as illustrated schematically in Figure 3.12. Also contained in Figure 3.12 are SEM images of the fracture surfaces of 0 DEA (a) and 1.5 DEA (b) samples. The modified sample fracture surfaces clearly show nano-scale cavities not present in the unmodified systems.

Evidence of stress relaxation was observed in the necked region after testing. In a separate study, drawn samples were annealed at room temperature, and above $T_g$ ($= 60 ^\circ$C). Samples annealed at room temperature deformed slightly, whereas the samples annealed above $T_g$ recovered their original shape. The shape recovering capacity of highly elongated samples suggest that covalent bond rupture was not prevalent during tensile deformation. This suggests that the improved ductility of the modified samples arises from enhanced molecular mobility associated with the disruption of weak interactions at the interfaces of the protovoids.

Average values of toughness and failure strain are shown for each batch of samples in Figures 3.13 and 3.14. Here, toughness refers to the total area under stress-strain curve to the point of fracture, and it is a measure of ductility. In addition, failure
strain is defined as the strain value at which the sample breaks. As can be seen in Figure 3.13, toughness increased with initial DCM content up to a solvent-to-monomer weight ratio of 0.75, beyond which no further increase is observed. The trend of failure strain was similar to that of toughness. Generally, thermoset toughness can be increased by using more flexible crosslinkers, but more flexible crosslinkers generally means lower $T_g$’s. We use relatively flexible Jeffamine crosslinkers, but across our values of solvent-to-monomer initial weight ratios, $T_g$ is essentially invariant while ductility is greatly enhanced. This demonstrates that the toughening effect due to the expansion of protovoids does not sacrifice $T_g$. In addition, Young’s modulus ($E$) and tensile strength at yield ($\sigma_y$) are listed in Table 3.3. The results show no significant statistical differences between unmodified and modified samples, demonstrating that the enhancement in ductility is obtained also without sacrificing Young’s modulus and tensile strength.
Figure 3.13. Average toughness values for each sample under uniaxial tensile load. Error bars indicate the distribution around statistical averages.
Figure 3.14. Average strain-at-failure values for each sample under uniaxial tensile load. Error bars indicate the distribution around statistical averages.
Table 3.3. Tensile properties (engineering) under uniaxial tensile load at room temperature.

<table>
<thead>
<tr>
<th>DEA</th>
<th>E (GPa)</th>
<th>$\sigma_y$ (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2.4 ± 0.2</td>
<td>34.6 ± 2.2</td>
</tr>
<tr>
<td>0.5</td>
<td>2.2 ± 0.2</td>
<td>32.0 ± 2.6</td>
</tr>
<tr>
<td>0.75</td>
<td>2.3 ± 0.1</td>
<td>38.9 ± 0.6</td>
</tr>
<tr>
<td>1</td>
<td>2.2 ± 0.1</td>
<td>35.7 ± 1.9</td>
</tr>
<tr>
<td>1.5</td>
<td>2.4 ± 0.1</td>
<td>31.9 ± 2.3</td>
</tr>
</tbody>
</table>
3.3.9. Void Size and Density

Raman et al.\textsuperscript{22} showed that in the RES technique using supercritical drying, average pores size of a nanoporous polymer network can be tailored through the initial solvent-to-monomer weight ratio. This suggests that the sizes of the protovoids generated using RESD would also increase with increasing solvent content and that the size might also be linked to improvement in ductility of the modified thermosets. Assuming that the features observed in the fracture surfaces of modified systems are indeed related to the size of the collapsed voids, protovoid size was investigated by quantitatively analyzing SEM micrographs of such surfaces. An image processing tool, ImageJ, was utilized to determine the average pore size and surface density. Figure 3.15 shows estimates of void diameters for samples from each batch. The error bars associated with each mean is the standard deviation obtained from at least three images at different surface locations. We observe that the average void diameter for the relatively circular features, with circularity of 0.3-1, is roughly 20-22 nm. According to Raman et al.\textsuperscript{22}, the average pores size of the nanoporous thermosetting networks obtained from 0.5 and 0.75 solvent-to-monomer weight ratios in RES was 2.4 and 3.2 nm. The features observed in our work are significantly larger perhaps because of deformation induced by loading.
Figure 3.15. Average pore diameter on the fractured surface vs. initial solvent-to-monomer weight ratio.
The question arises as to whether the observed voids were present before failure. The following discussion serves to answer this question. The surface area fraction occupied by voids was obtained from the images of modified and unmodified systems. These data are reported in Figure 3.16. For the modified samples broken at ambient temperature void area fractions were not substantially different ranging between 0.5 and 1.2%. If it is assumed that these voids were present before mechanical testing, the area void fractions to calculate density values using the equation below:

\[ \rho_2 = (1 - \alpha) \times \rho_1 \]  

(3.3)

where \( \rho_2 \) is predicted density, \( \rho_1 \) is the unmodified epoxy density, and \( \alpha \) is void-covered area fraction which was measured through image processing of the micrographs. For instance, 1.5 DEA was found to have an average \( \alpha \) value of 1.05% from fracture surface micrographs. This yields a predicted density of approximately 1.114 g/cm³. This value is significantly below the average density of the material prior to tensile deformation. Thus this supports the hypothesis that voids are not pre-existent but a result of protovoid opening and deformation during fracture.
In order to further test this hypothesis, 1.5 solvent-to-monomer weight ratio samples were fractured at liquid nitrogen temperature. This time very few voids were observed using SEM as shown in Figure 3.17 in which images of cold-fracture and RT-fracture surface morphology for two identical samples are presented. The quantitative measurement of void surface coverage is given in Figure 3.16 (1.5 DEA-FF) and strongly supports that freeze fractured morphology of the 1.5 DEA sample resembles the RT fracture surface morphology of 0 DEA samples and not that of the 1.5 DEA RT fracture surface (as shown by arrows in Figure 3.16). The reduced number of visible voids in cold-fracture surface could be due to the speed of crack propagation in cold environments. Experimental studies showed that for viscoelastic materials, a crack propagates faster in a colder environment leading to a reduced value of critical stress intensity factor (K_{ic}). Therefore, in colder fracture, the protovoids do not have sufficient time to expand in response to tensile deformation, so fewer holes will be observed on cold-fracture surface micrographs. These results support the conclusion that the observed pores are a result of the fracture event.
Figure 3.16. Average surface area covered by voids for RT-fracture surfaces (0 DEA, 0.5 DEA, 0.75 DEA, 1 DEA and 1.5 DEA) and freeze-fracture surfaces (1.5 DEA-FF).
Figure 3.17. Surface morphology of the modified sample, 1.5 DEA. Freeze-fracture (a) and RT-fracture surface (b). Scale bars are both 1 µm lengthwise.
3.3.10. Compressive Properties

The use of data from compression testing is sometimes preferred because phenomena such as crazing and necking are suppressed.\textsuperscript{45} Therefore, to better understand the effect of the protovoids on compressive behavior of the modified thermosets, the response of those materials to uniaxial compressive load was investigated. In this case true stress-strain values were utilized instead of the engineering convention, since the dimensions of the samples greatly vary during the test. True stress-strain values were evaluated from the engineering stress-strain based on the following equations:\textsuperscript{46}

\[ \sigma_t = \sigma_e (1 + \varepsilon_e) = \sigma_e \lambda \] \hspace{1cm} (3.4)

\[ \varepsilon_t = \ln(1 + \varepsilon_e) = \ln \lambda \] \hspace{1cm} (3.5)

Here, \( \lambda \) is the extension ratio which is defined by \( \lambda = L/L_0 \), \( \sigma_t \) and \( \varepsilon_t \) are the true stress and true strain, respectively, and \( \sigma_e \) and \( \varepsilon_e \) are the corresponding engineering values. True stress vs. (1-\( \lambda \)) for a typical unmodified sample, 0 DEA, and a modified, 1.5 DEA, are shown in Figure 16.
Figure 3.18. True stress vs. (1-λ) for unmodified, 0 DEA, (solid black line) and modified, 1.5 DEA, (red dashed line) in compressive mode.
Values of compressive modulus ($E$), yield strength ($\sigma_y$), and compressive strength ($\sigma_c$) based on true stress and strain are listed in Table 3.4. Results show no significant statistical differences of compressive moduli, compressive strength and compressive yield strength as a function of sample type. This suggests that induced protovoids do not sacrifice the load bearing capacity of the network structures. Also shown in Table 4 are the engineering failure strain ($\varepsilon_f$) and plastic deformation ($\varepsilon_r - \varepsilon_y$) for the series of samples showing that unmodified systems possess significantly lower failure strain and plastic deformation capacity. Thus the modified systems absorb significantly more energy before failure in a manner consistent with the observations obtained from tensile experiments.
<table>
<thead>
<tr>
<th>DEA</th>
<th>E (GPa)</th>
<th>( \sigma_y ) (MPa)</th>
<th>( \sigma_r ) (MPa)</th>
<th>( \varepsilon_r ) (%)</th>
<th>( \varepsilon_r - \varepsilon_y ) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 DEA</td>
<td>1.6 ± 0.1</td>
<td>48.7 ± 3.8</td>
<td>138.9 ± 13.1</td>
<td>70.3 ± 2.1</td>
<td>62.9 ± 1.4</td>
</tr>
<tr>
<td>0.5 DEA</td>
<td>1.6 ± 0.2</td>
<td>48.9 ± 5.3</td>
<td>141.9 ± 20.1</td>
<td>79.4 ± 3.5</td>
<td>70.3 ± 3.5</td>
</tr>
<tr>
<td>0.75 DEA</td>
<td>2.0 ± 0.3</td>
<td>58.6 ± 4.9</td>
<td>185.5 ± 51.1</td>
<td>84.4 ± 3.7</td>
<td>76.4 ± 1.5</td>
</tr>
<tr>
<td>1 DEA</td>
<td>1.7 ± 0.2</td>
<td>46.4 ± 6.0</td>
<td>160.7 ± 25.0</td>
<td>85.4 ± 3.4</td>
<td>77.1 ± 2.4</td>
</tr>
<tr>
<td>1.5 DEA</td>
<td>2.1 ± 0.2</td>
<td>54.5 ± 6.7</td>
<td>175.0 ± 80.2</td>
<td>86.2 ± 5.4</td>
<td>79.7 ± 4.3</td>
</tr>
</tbody>
</table>

Table 3.4. Compressive properties of 0, 0.5, 0.75, 1 and 1.5 DEA samples.
3.4. Conclusions

More ductile crosslinked thermosets are obtained by applying a novel processing technique termed reactive encapsulation of solvent/drying, or RESD. SEM images from the fracture surfaces showed clear voids on the modified samples whereas prior to tension, all modified samples had the same density, $T_g$, Young’s modulus of the unmodified epoxy. Modified samples also had the same ultimate tensile strength but much higher ductility compared to the unmodified epoxy. It was shown using all-atom simulations that during-cure solvent species alter the polymer network topology. The presence of distinct topological features in the modified network is likely the origin of the large improvement in ductility. Topology-based toughening is potentially an important step toward developing better high performance network polymers and composites. Unlike other toughening methods, critical mechanical and thermal properties such as Young’s modulus, ultimate tensile strength and glass transition temperature are not sacrificed.

3.5. List of References


Chapter 4. Porous Polymer Network Structures; Synthesis and Characterization

4.1. Introduction

In the previous Chapter it was shown that the behavioral characteristics of epoxy thermosets can be linked to the molecular structure and topology of the polymer networks.\textsuperscript{1, 2} Other studies have shown that many of the excellent properties of epoxy materials are due to their densely crosslinked nature.\textsuperscript{3, 4} One fundamental parameter used to quantify polymer network structure is the molecular weight between crosslinks, $M_c$.\textsuperscript{5, 6} Among techniques used to elucidate $M_c$, the two well-defined methods are those based on equilibrium swelling theory,\textsuperscript{7} and rubber-elasticity theory.\textsuperscript{8, 9} Equilibrium swelling theory, which will be discussed in this Chapter, was introduced by Frenkel.\textsuperscript{10} It was later investigated and established by Flory-Rehner\textsuperscript{11, 12} and was further developed by Dusek,\textsuperscript{13, 14} and Bray-Merrill.\textsuperscript{15} The classical equilibrium swelling theory is extensively used to characterize the network structure of the hydrogels prepared in water,\textsuperscript{16, 17} or the systems that are free-radical crosslinked.
Although the equilibrium swelling technique is a very reliable method to measure values of molecular weight between crosslinks for dense polymer network structures or for those prepared in moderately dilute environments, our experimental results show that crosslinked gels that are formed in very dilute solutions, such as the ones studied by Raman et al.,\textsuperscript{18} have $M_c$ values, measured via equilibrium swelling, that deviate from those of the dense polymer networks.

The principal objective of the study in this Chapter is to employ equilibrium swelling to investigate and characterize the network structure of crosslinked polymers that are formed/cured in dilute environments, i.e. in presence of excess inert solvent during cure. Experimental studies revealed that highly nanoporous structures are obtained when the during-cure solvent is removed from the polymer networks via supercritical extraction/drying.\textsuperscript{18}

The well-known Dusek equation was used in this study to calculate the $M_c$ values of polymer networks that are formed over a range of solvent inclusion. The measured $M_c$ values were compared to the glass transition temperature of corresponding dried gels. It was observed that, at high solvent contents, $M_c$ and $T_g$ values do not fit the well-known Fox and Loshaek equation. It was shown that the discrepancy can be resolved by adjusting the Dusek equation via incorporation of a factor that allows the equation to be applicable for highly nanoporous crosslinked
polymer structures. The adjusted values of molecular weight between crosslinks for a series of supercritically dried epoxy polymers were determined via the modified equation and the results compared to the corresponding $T_g$ values. It was shown that for the gels that are formed in very dilute environments, the modification to the Dusek equation provides $M_c$ values that are consistent with $T_g$ behavior obtained via the Fox and Loshaek equation. This was not the case when the non-adjusted values of $M_c$ were used.

4.2. Experimental

4.2.1. Materials

DGEBA (Miller-Stephenson) of three different molecular weights (EPON-828, EPON-836, and EPON-1001F) was used as the epoxy resin. A cycloaliphatic tetra-functional diamine, 4,4’-methylenebiscyclohexanamine, (PACM, Air Products) was used as the curing agent, and ultrapure tetrahydrofuran, THF (Sigma-Aldrich), was used as the inert solvent. Table 4.1 lists the chemical structures of the materials used in this study and their average molecular weights.
Table 4.1. Chemical structures of the materials used in this study.

<table>
<thead>
<tr>
<th>Type</th>
<th>Product Name</th>
<th>Chemical Structure</th>
<th>Molecular Weight (g/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Epoxy resin</td>
<td>EPON-828 (n=0.13)</td>
<td><img src="image" alt="Chemical Structure" /></td>
<td>376</td>
</tr>
<tr>
<td></td>
<td>EPON-836 (n=0.98)</td>
<td><img src="image" alt="Chemical Structure" /></td>
<td>625</td>
</tr>
<tr>
<td></td>
<td>EPON-1001F (n=2.5)</td>
<td><img src="image" alt="Chemical Structure" /></td>
<td>1075</td>
</tr>
<tr>
<td>Curing agent</td>
<td>PACM</td>
<td><img src="image" alt="Chemical Structure" /></td>
<td>210</td>
</tr>
<tr>
<td>Solvent</td>
<td>THF</td>
<td><img src="image" alt="Chemical Structure" /></td>
<td>72</td>
</tr>
</tbody>
</table>
4.2.2. Sample Preparation

The purity of the DGEBA resins was confirmed by GPC. PACM was used as received. Stoichiometric amount of epoxy resin and the curing agent (2:1 molar ratio), were mixed with specific amounts of the solvent (THF) in a Thinky mixer until a clear transparent liquid was obtained. In order to reduce the amount of THF evaporation, the screw threads were lined with non-adhesive Teflon® tape before closing the vial. Sample batches were delineated by THF to Epoxy-Amine resin weight ratio. For instance, a “1 TEA” sample has an equal weight of solvent to resin monomers and so has 50% solvent by weight. Batches with TEA’s of 0, 0.2, 0.5, 1, 1.5, 2, 3, 4, 6, and 8 were produced for systems made from EPON-828 and EPON-836. Batches with TEA’s of 0, 0.2, 0.5, 1, 1.5, 2, 3, and 4 were prepared for the systems composed of EPON-1001F.
Table 4.2. Curing time at 60 °C for samples with different THF content (regardless of the type of epoxy resin). The asterisked sample (0 TEA) was post-cured at 160 °C for 12 hrs.\textsuperscript{19}

<table>
<thead>
<tr>
<th>Sample</th>
<th>Curing time (h) at 60 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 TEA*</td>
<td>4</td>
</tr>
<tr>
<td>0.2 TEA</td>
<td>~96</td>
</tr>
<tr>
<td>0.5-1 TEA</td>
<td>~168</td>
</tr>
<tr>
<td>1.5-2 TEA</td>
<td>~336</td>
</tr>
<tr>
<td>3 TEA</td>
<td>~672</td>
</tr>
<tr>
<td>4-6 TEA</td>
<td>~1344</td>
</tr>
<tr>
<td>8 TEA</td>
<td>~2016</td>
</tr>
</tbody>
</table>
4.2.3. Curing

The mixtures were placed at 60 °C ± 1 °C for sufficient time to attain close to full conversion in the presence of the inert solvent. Conversion was monitored by tracking the FTIR absorbance peak (in the near IR region) associated with oxirane bands at 4530 cm\(^{-1}\), and the peak associated with N-H bands at 5056 cm\(^{-1}\) and 6510 cm\(^{-1}\).\(^{20, 21}\) To ensure fully reacted systems were obtained at the curing temperature, the samples were kept at the curing conditions for the durations as listed in Table 4.2. FTIR spectra of the specimens after cure did not show the existence of the peaks attributed to epoxy and amine bands, suggesting the complete conversion. The batches composed of EPON-1001F at very high THF contents (6 TEA and 8 TEA) never gelled at the curing temperature of 60 °C, and thus they were excluded from further analysis.

4.2.4. Equilibrium Swelling Experiment

Once fully reacted gels were prepared, equilibrium swelling experiments were conducted by weighing a small cut of each gel, \(W_r\), and immersing it in a vial containing THF. The vials were capped and maintained at 60 °C for two days and
subsequently at room temperature for one week. The mass uptake was recorded until an equilibrium weight was achieved.

4.2.5. Supercritical Solvent Extraction

Supercritical drying procedure was conducted using a SPI-DRY™ CPD Supercritical Fluid Extraction System. The apparatus consists of a chamber where liquid CO₂ can be stored. The temperature of the whole system can be controlled by immersing the entire pressurized system in a water bath. Wet samples, prepared in presence of solvent, were immediately placed inside the chamber, and then the chamber was filled with liquid CO₂ until the sample was entirely immersed in liquid CO₂, allowing the THF to be replaced by CO₂. Samples remained in liquid CO₂ for sufficient time to allow the solvent exchange process to be completed, and then the chamber was refilled with fresh liquid CO₂. The chamber was maintained at 5-10 °C during this step. The solvent exchange process was repeated three to four times. The chamber temperature was raised above the supercritical temperature of CO₂, (31.1 °C). Supercritical CO₂ was then gradually vented. Once all CO₂ was exhausted, dried samples were obtained.
4.2.6. Differential Scanning Calorimetry

A Perkin Elmer Differential Scanning Calorimeter model DSC-7 was used to measure glass transition temperature. All samples were tested through a heat/cool/heat cycle for 3 cycles, in the temperature range of 30 °C to 200 °C with a scanning rate of 10 °C/min. Values of glass transition temperature were measured from the second order transition (the inflection point) in the third cycle. The DSC thermographs are shown in Appendix B.

4.3. Results and Discussion

4.3.1. Equilibrium Swelling Analysis

A swelling test was performed on wet samples to measure the value of molecular weight between crosslinks based on the Dusek swelling theory. First, the equilibrium volume fraction of each phase, solvent (THF), phase 1, and polymer network (PN), phase 2, was measured in the relaxed state (immediately after crosslinking but before swelling) as follows:
where $v_{1r}$ and $v_{2r}$ are the volume fractions of the solvent and PN in relaxed state, respectively. The quantities $\rho_{PN}$ and $\rho_{THF}$ are the corresponding densities of PN (1.26 g/cc) and THF (0.899 g/cc). The quantity $w_{2r}$ is the weight fraction of PN in the gel, and it is assumed to be equal to the monomer weight fraction in the mixture. This assumption is only valid if the monomers polymerize to high conversions where formation of sol fraction in the gels is reduced. At the end of polymerization, FTIR spectra did not show any epoxy or primary amine peaks for the gels, implying that the monomer resins achieved high reaction conversions. Therefore, volume fractions of solvent and PN at equilibrium swollen state, $v_{1s}$ and $v_{2s}$, were computed as:

$$v_{2s} = \frac{w_{2r} \rho_{PN}}{w_{2r} \rho_{PN} + (1 - w_{2r}) \rho_{THF}}$$  \hspace{1cm} (4.3)

$$v_{1s} = 1 - v_{2s}$$  \hspace{1cm} (4.4)

where $W_r$ and $W_s$ are the total weights of the gels in relaxed and swollen state.
At least three experiments were conducted for each system, and the average values of $v_{1r}$, $v_{2r}$, $v_{1s}$, and $v_{2s}$ are reported in Table 4.3.\textsuperscript{22}
Table 4.3. Average values of $v_{1r}$, $v_{2r}$, $v_{1s}$, and $v_{2s}$ for each system.²²

<table>
<thead>
<tr>
<th>THF : epoxy-amine wt. ratio (TEA)</th>
<th>Vol. fraction of THF in the relaxed gel, $v_{1r}$</th>
<th>Vol. fraction of PN in the relaxed gel, $v_{2r}$</th>
<th>Vol. fraction of THF in the swollen gel, $v_{1s}$</th>
<th>Vol. fraction of PN in the swollen gel, $v_{2s}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Epon-828</td>
<td>Epon-836</td>
<td>Epon-1001F</td>
<td>Epon-828</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0.383</td>
<td>0.415</td>
</tr>
<tr>
<td>0.2</td>
<td>0.221</td>
<td>0.779</td>
<td>0.449</td>
<td>0.483</td>
</tr>
<tr>
<td>0.5</td>
<td>0.415</td>
<td>0.585</td>
<td>0.552</td>
<td>0.575</td>
</tr>
<tr>
<td>1</td>
<td>0.586</td>
<td>0.414</td>
<td>0.65</td>
<td>0.666</td>
</tr>
<tr>
<td>1.5</td>
<td>0.68</td>
<td>0.32</td>
<td>0.699</td>
<td>0.733</td>
</tr>
<tr>
<td>2</td>
<td>0.739</td>
<td>0.261</td>
<td>0.741</td>
<td>0.767</td>
</tr>
<tr>
<td>3</td>
<td>0.81</td>
<td>0.19</td>
<td>0.787</td>
<td>0.818</td>
</tr>
<tr>
<td>4</td>
<td>0.85</td>
<td>0.15</td>
<td>0.836</td>
<td>0.849</td>
</tr>
<tr>
<td>6</td>
<td>0.895</td>
<td>0.105</td>
<td>0.887</td>
<td>0.893</td>
</tr>
<tr>
<td>8</td>
<td>0.919</td>
<td>0.081</td>
<td>0.915</td>
<td>0.916</td>
</tr>
</tbody>
</table>
4.3.2. Molecular Weight between Crosslinks

The classical equilibrium swelling equation was used in this study to measure the values of molecular weight between crosslinks, $M_c$, for the resulting polymer networks. Accordingly, the average molecular weight between crosslinks for a gel that formed in the presence of a solvent is quantified by:

$$\frac{1}{M_c} = 2 - \frac{v_p}{V_1} \left[ \ln(1 - v_{2s}) + v_{2s} + \chi_1 v_{2s}^2 \right] v_{2r} \left[ \left( \frac{v_{2s}}{v_{2r}} \right)^{1/3} - \frac{1}{2} \left( \frac{v_{2s}}{v_{2r}} \right) \right]$$

Here, $\bar{M}$ is the primary molecular weight, and according to Flory this quantity approaches to infinity for a perfect network. Additionally, $M_c$ is the average molecular weight between crosslinks, $V_1$ is the molar volume of the solvent phase, $v_p$ is the specific volume of the polymer phase, and $\chi_1$ is the Flory-Huggins parameter, which is the only material-specific parameter that characterizes the interaction energy between solute (PN) and solvent (THF) species.

For a highly crosslinked polymer networks, such as the cases for amine-cured epoxy systems, the quantity $\bar{M}$ is much greater than $M_c$ under a high degree of polymerization, and hence equation (5) can be rewritten as:
\[
\bar{M}_c = -\frac{v_{2r} \left[ \left( \frac{v_{2s}}{v_{2r}} \right)^{1/3} - \frac{1}{2} \left( \frac{v_{2s}}{v_{2r}} \right) \right]}{\frac{V_p}{V_1} \left[ \ln(1 - v_{2s}) + v_{2s} + \chi_1 v_{2s}^2 \right]}
\]

(4.6)

The Flory-Huggins interaction parameter, \( \chi_1 \), was estimated using the Hansen solubility parameter calculations based on group contribution method.\(^{23}\) According to the chemical structures of the PN repeating unit and THF, this quantity was found to be 0.424 for the systems at 25 °C.

Values of \( M_c \) for the three DGEBA systems i.e. Epon828-PACM, Epon836-PACM, and Epon1001F-PACM were measured using eqn. (4.6) and plotted against initial solvent content in Figure 4.1. The results for the three systems investigated indicate that the average values of molecular weight between crosslinks deviate from those of the dense systems. The deviation is slight and negligible until 20% volume fraction of solvent is reached. This deviation increases slightly in more dilute environments, up to 60% volume fraction of solvent. However, for systems above 60% volume fraction of solvent, \( M_c \) values increase dramatically indicating that either the molecular structure of the polymer networks is significantly changing, or the model is not adequate to predict the behaviour of swelling when polymer networks are formed with extremely high solvent content.
Figure 4.1. Values of molecular weight between crosslinks based on Dusek model.²²
An investigation of the influence of initial solvent content on dry density and $T_g$ was conducted to determine if the polymer networks are significantly altered resulting in much higher $M_c$ values.

Density measurements indicate that porous aerogels are formed when the solvent in the wet gels is supercritically extracted, as shown by Raman et al. However, it was observed that the density of the supercritically dried aerogels increased with thermal drying as the pores collapse. For example, the density of Epon828-PACM (8 TEA) increased from 0.3 gr/cc to 1.2 gr/cc upon thermal treatment. The density of the aerogel after annealing above $T_g$ was comparable to that of the dense polymer networks (0 TEA, Epon828-PACM). Figure 4.2 is a schematic representation of the probable state of the polymer network structure at each stage of processing. The increase in density upon thermal treatment suggests that the pore structures that were formed upon supercritical extraction/drying collapse completely. These fully cured networks have similar densities to those of systems prepared without solvent, but with nonbonded molecular surfaces, which are network topological differences. This concept was scrutinized earlier in Chapter 3, as well as the published works by Jang et al. and Sharifi et al.
4.3.3. Thermal Analysis.

The values of glass transition temperature for the supercritically dried samples, aerogels, were measured using a DSC. Accordingly, the average $T_g$ values and their associated error bars (from at least three replicates) for each system are shown in Figure 4.3.

The results in Figure 4.3 indicate that the value of glass transition temperature for each polymer type is not significantly affected by the solvent content during cure. In a highly crosslinked polymer, $T_g$ is a measure of segmental mobility of the polymer chains and thus can be related to the crosslinking density or molecular weight between crosslinks. However, it cannot elucidate the differences between porous and dense structures.

For the aerogels (TEA > 0), a slight deviation in $T_g$ values from the dense polymer structures (TEA = 0) was observed. The difference in glass transition temperature between the dense polymer networks and the aerogels is primarily due to residual solvent permanently trapped in the aerogels. The hydrogen-bonding between the existing hydroxyl groups and the oxygen in THF molecules prevent the solvent from freely leaving the systems. This phenomenon is slightly moderated for the loosely crosslinked polymer networks, such as the ones with Epon836-PACM and Epon1001F-PACM.
Figure 4.2. Probable states of: (a) Dense polymer network structure (0 TEA), (b) Fully reacted polymer network structure in presence of THF, (c) Fully reacted polymer network structure after supercritical extraction/drying, (d) Fully reacted polymer network structure after thermal treatment.
Figure 4.3. Glass transition temperature values for the super-critically dried samples. x-axis is the volume fraction of solvent in the gels prior to super-critical extraction/drying.
As discussed, the aerogels that are cured with higher solvent inclusion form polymer network structures with higher porosity. The increased porosity facilitates the residual solvent species leaving the system in first DSC heating cycle. This might be the reason for the apparent increase in $T_g$ values for all the systems at $v_{1r}$ above 0.6. This increase in $T_g$ is highlighted in Figure 4.3.

There is a clear difference in average $T_g$ values for each system due to molecular size of the resin. In accordance with the Fox and Loshaek equation, thermosets made from resins with larger molecular weight typically have lower crosslinking density. Under such conditions, the local mobility of polymer chains is higher, and thus $T_g$ values are lower for the crosslinked systems.

Generally, for highly crosslinked polymers, glass transition temperature is related to the molecular size entrapped between crosslinks as expressed by the Fox and Loshaek equation:

$$T_g = T_{g\infty} + \frac{\xi}{M_c} \quad (4.7)$$

Here, $T_{g\infty}$ is the glass transition temperature of the elastic chain backbone at infinite molecular weight, and $\xi$ is proportional to the molecular weight of the monomer resins and the molar ratio of the epoxy resin to the curing agent. In this study, both $T_{g\infty}$ and $\xi$ are unique and constant for each of the systems. For a crosslinked
polymer, this equation states that the higher the molecular size between crosslinks, the lower the $T_g$ should be.

Figure 4.4 shows the glass transition temperature vs. molecular weight between crosslinks, $M_c$, predicted by Dusek model. The results indicate that, for the three systems, $T_g$ values are insensitive to the molecular weight between crosslinks. This is not in accordance with the predicted behavior illustrated by the Fox and Loshaek equation described above. This discrepancy suggests that the Dusek equation is inadequate for measuring the $M_c$ values of crosslinked epoxy polymers formed in highly dilute environments.

4.3.4. Modification to the Dusek model

Dusek described polymer network structures based on Flory’s description of crosslinked systems. Flory visualized polymer networks as meshes that are characterized by their number of elastic chains ($\nu$). As discussed earlier, the model does not predict the elastic behavior of gels prepared in very dilute environments. Unlike structures prepared in the absence of solvent, elastic chains cannot be found everywhere in the solvent-based systems. In fact, the elastic behavior of porous networks that contain significant pore volume occupied by solvent is different than that of dense structures. Therefore, a factor is introduced in the development of the
Dusek equation that takes into account the probability of finding an elastic chain in the entire volume of the gel (PN + solvent). Since all elastic chains are part of the polymer phase, this probability is at least equal to the probability of finding PN in the gel. This probability term is defined in the equation below.

\[
P_v = \frac{vol.PN \ (V_{PN})}{vol.\ PN \ (V_{PN}) + vol.\ solvent \ (V_s) + \ free \ vol.\ (V_f)} \quad (4.8)
\]
Figure 4.4. Glass transition temperature vs. molecular weight between crosslinks (measured by the Dusek model).
The free volume in a gel is generally expected to be much lower than the volume of the gel \(V_f \ll V_{PN} + V_s\); hence, neglecting the \(V_f\) term, the simplified expression is equal to the volume fraction of PN in relaxed gel.

\[
P_v = \frac{vol.\,PN \,(V_{PN})}{vol.\,PN \,(V_{PN}) + vol.\,solvent \,(V_s)} = \nu_{2r}
\]  

(4.9)

In the limit of low solvent inclusion, where volume of solvent is much smaller than the volume of PN \(V_s \ll V_{PN}\), the probability factor, \(P_v\), becomes unity, and the effect of porosity is neglected. This was consistent with our observations of \(\nu_{1r} < 0.2\) in Figure 4.1. By incorporating this concept into the traditional development of the Dusek equation, 4.10 is obtained. Mathematical derivation of equation (4.10) is shown in Appendix A.

\[
M_c = -\frac{\nu_{2r}}{V_1} \left[ \frac{\nu_{2s}}{\nu_{2r}} \left( \frac{1}{3} - \frac{1}{2} \frac{\nu_{2s}}{\nu_{2r}} \right) \right] \ln(1 - \nu_{2s}) + \nu_{2s} + \chi_1 \nu_{2s}^2
\]  

(4.10)

The values of molecular weight between crosslinks for each of the gel samples previously discussed were measured based on the modified Dusek model and plotted vs. solvent content in relaxed state, \(\nu_{1r}\), as shown in Figure 4.5. In this case, the molecular weight between crosslinks is relatively constant for each polymer system. This result supports the contention that the molecular structure of the
polymer (molecular weight between crosslinks) is not altered by the presence of the solvent, but rather that the changes that occur pertain primarily to rearrangement of the network topology.

In Figure 4.6, the glass transition temperature of the dried polymer phase for each of the gels is plotted against the adjusted $M_c$ values. The results indicate that the effect of initial solvent content on $T_g$ and $M_c$ is minimal. In addition, the new $M_c$ values can be used to predict the $T_g$ values via Fox and Loshaek equation, suggesting that the adjusted Dusek model (shown in eqn. 4.10) is adequate for use in predicting the approximate values of molecular weight between crosslinks for the systems produced in highly dilute environments.
Figure 4.5. Values of molecular weight between crosslinks based on the modified Dusek model.22
4.3.5. Effect of network structure on equilibrium swelling

According to Flory’s theory of mixing for crosslinked polymers,\textsuperscript{12} the favorable interaction between polymer chains and fluid molecules allows a spontaneous mixing/swelling to occur. However, as this mixing process goes forward, a retractive force develops from the elastic nature of polymer chains that opposes the swelling process. A state of equilibrium is reached when configurational entropy associated with elastic retractive force and favorable interactions between solvent species and the polymer chains provide minimum free energy for the system. Figure 4.7 shows the equilibrium volume fraction of THF in the swollen state vs. the corresponding quantity in relaxed state (as prepared). The increasing trend for equilibrium volume fraction in the swollen state implies that the gels that are formed in more dilute solutions have higher swelling capacity. This effect is only attributed to the polymer network topology where presence of an inert solvent during cure could affect the substitution factor $k_2/k_1$,\textsuperscript{21} or restrict the local directions in which crosslink bonds can form.\textsuperscript{1, 2} In either case, fully cured polymer networks with altered network topologies are forming that are capable of swelling more than the corresponding dense structures.
Figure 4.6. Glass transition temperature vs. adjusted molecular weight between crosslinks.\textsuperscript{22} (measured by eqn. 4.10)
It was also observed that the equilibrium volume fraction of solvent in the swollen state for the Epon1001F-PACM is higher than that of the Epon836-PACM and Epon828-PACM. This observation can be explained by the crosslinking density and $M_c$ values. In fact, Epon1001F has a larger molecular weight than the other two epoxy resins and thus creates polymer networks with looser crosslinking density, or higher molecular weight between crosslinks, as shown in Figure 4.5. Therefore, the elastic retractive force is alleviated for this system relative to the other systems leading to more solvent swelling capacity.

Additionally, it was observed that the difference between equilibrium solvent uptakes in swollen state is alleviated as the during-cure solvent content, $v_{1r}$, increases. This difference is negligible for the gels prepared in very dilute environments such as the ones with $v_{1r} > 0.8$. The results in Figure 4.7 suggest that equilibrium solvent uptake for the thermosets that are cured in very dilute environments ($v_{1r} > 0.8$) are controlled by a nodular distance other than molecular weight between crosslinks because the opposing elastic retractive forces seem to be comparable regardless of the resin type. According to the concept of the “topological distance”, which was introduced in Chapter 3 and the published work by Sharifi et al.\textsuperscript{2} elastic properties of polymer networks cured in the presence of excess inert solvent can be determined by this quantity. As proposed, since at high solvent contents, this quantity is much larger than the size of $M_c$ for a homogeneous
polymer network, it explains why the difference between equilibrium solvent uptakes is mitigated with the increase of $v_{1r}$. In fact, in this case, the elastic retractive force is dominantly determined by topological distance rather than $M_c$. This concept is pointed out in Figure 4.7.
Figure 4.7. The equilibrium volume fraction of THF in swollen state vs. relaxed state (as prepared).
4.4. Conclusion

Equilibrium swelling and glass transition temperature were used to characterize polymer network structures that were cured in the presence of an inert solvent. Three different epoxy resins with varying molecular sizes were cured with the same curing agent. According to the Dusek equation, the equilibrium solvent uptake suggests that during cure the inert solvent species affects polymer network structures by increasing the molecular weight between crosslinks for the very dilute samples, $v_{1r} > 0.8$. However, $T_g$ values of the resulting aerogels (based on the Fox and Loshaek equation) were not consistent with the observed $M_c$ values. The discrepancy suggests that the Dusek equation is inadequate to measure the $M_c$ values for crosslinked polymers when cured in highly dilute environments. The model was adjusted by incorporating probabilistic factor, $P_v$, based on the probability of finding an elastic chain in the porous structure. Consequently, the $T_g$ values could be predicted by the new $M_c$ values via the Fox and Loshaek equation. The results imply that the values of molecular weight between crosslinks are insensitive to the amount of solvent present during cure and in fact, the solvent species create pore structures throughout the entire polymer network and alter network topology.
4.5. List of References


10. Frenkel, J. Rubber Chemistry and Technology 1940, 13, (2), 264-274.


Chapter 5. Synthesis and Characterization of Polymer Network Isomers using Diamine-functionalized Partially Reacted Substructures (dPRS)

5.1. Introduction

Topology-based toughening was introduced and developed in Chapter 3. It was shown that the mechanical performance, particularly ductility, of an epoxy thermosetting system can be substantially adjusted without degrading other essential properties such as strength, modulus, and Tg. However, the use of solvent and the drying and annealing stages of the RESD method limit its applicability to small parts with thin cross-sections. Finding a solvent-free methodology that grants synthesis of samples at larger quantities is essential in order to scale-up topology-based toughening as a reliable method that could compete with other existing toughening methods such as: di-block copolymers,\(^1\) tri-block copolymers,\(^2\) interpenetrating networks,\(^3\) core/shell particles,\(^4\) rubber particles,\(^5\) elastomers,\(^6\) as well as incorporation of thermoplastics,\(^7\)\(^,\)\(^8\) titania, alumia,\(^9\) silica,\(^10\) graphene platelets,\(^11\) carbon-nanotubes,\(^12\) fullerene,\(^13\) POSS,\(^14\) etc.

Within the study in this Chapter, it was demonstrated that the toughening of a thermosetting epoxy system through the rearrangement of network topology,
creates network isomers that possess the same overall composition but have concomitantly improved fracture toughness and $T_g$. This work is motivated by the recently proposed and novel approach to toughening thermosets demonstrated through a series of coarse-grained molecular simulations,\textsuperscript{15,16} which suggested that upon tensile extension, a void-opening or surface-drawing mechanism in highly crosslinked polymers enhances the material’s ductility without affecting tensile strength. The fundamentals of this study, similar to the discussions in Chapter 3 and Sharifi et al.\textsuperscript{17}, is to embed nano-structures in the polymer networks that could mimic the role of the molecular surfaces (or “protovoids”), without using solvent. The void-opening mechanism improves material ductility and toughness without affecting yield strength, modulus and even $T_g$, yet the new method for controlling the network topology does not rely on the use of a solvent so that it can be widely applied in industrial settings.

The method, termed the “Partially Reacted Substructure (PRS)” method, involves sub-gel partial curing of a relatively low-$T_g$ diamine/epoxy system followed by its blending and complete curing in a high-$T_g$ diamine/epoxy system while maintaining overall stoichiometry. Network isomers are therefore prepared by varying the degree of cure for the low-$T_g$ diamine/epoxy system (PRS) before it is co-reacted with the high-$T_g$ monomers. The base isomer for comparison is prepared by mixing all reactants without pre-reaction. PRS overcomes the
limitation of RESD in that it does not involve sacrificial solvent, thereby allowing fabrication of samples of any size and geometry, and enabling measurement of plane-strain fracture toughness using linear elastic fracture mechanics (LEFM). We demonstrate significant toughness improvements using the PRS method without sacrificing strength and with increased $T_g$. We further demonstrate that the degree of toughness enhancement is correlated to the degree of partial curing.

5.2. Experimental

5.2.1. Materials

Diglycidyl ether of bisphenol-A (DGEBA, EPON 825 – Miller-Stephensen), $n=0.07$, was used as the epoxy resin. In addition, poly(propylene-oxide)diamine (PPODA, Jeffamine D-series – Huntsman), $x=33$, $x=68$, and diethyltoluenediamine (DETDA, EPIKURE W – Miller-Stephensen) were used as the curing agents. The molecular structures of these materials are shown in Figure 5.1.
**Figure 5.1.** Molecular structure of the epoxy resin and the curing agents used in this study. (a) EPON 825 (DGEBA), n=0.07, (b) Jeffamine D-4000 (PPODA), x=68, and Jeffamine D-2000 (PPODA), x=33, (c) EPIKURE W (DETDA).
5.2.2. Synthesis Procedure

The formulation of the polymer isomers involved three basic steps: (1) Synthesizing the Partially Reacted Substructures (PRS) with controlled extent of polymerizations; (2) making blends of blank epoxy (DGEBA + DETDA) with specific contents of the reactive PRS; and (3) curing the blends.

PRS was produced by adding/mixing stoichiometric blends of PPODA and DGEBA at 80 °C. The chemical conversion of these mixtures was monitored using a Nexus 870 FTIR spectrometer (Thermo Nicolet Corp.) in the near IR region. Figure 5.2(a) shows representative FTIR spectra taken over a period of time for this reaction. The peak at 4530 cm\(^{-1}\) corresponds to the stretching and bending of oxirane bands, and the peak at 4930 cm\(^{-1}\) corresponds to the NH\(_2\) combination bands.\(^{18,19}\) The decrease of epoxy and amine concentrations signifies the presence of epoxy-amine reactions. Figure 5.2(b) shows the fractional conversion of epoxy with respect to time obtained using the epoxy peak area.

Cure was stopped at 60%, 70%, and 80% conversion as shown in Figure 5.2(b) by cooling to room temperature. The resulting PRS samples were labelled 60%, 70% and 80% conversion PRS, respectively. Specific amounts of the each of the resulting PRS were then added to stoichiometric blends of DGEBA and DETDA to make
solutions of 10%, 15%, and 20% by weight of PRS. The cured samples were called PRS-modified samples and were labelled according to their PRS chemical conversion. Additionally, batches with 10%, 15%, and 20% by weight of PRS were prepared without PRS reaction taking place (i.e. 0% conversion). The resulting cured samples were called PRS-control samples (labelled “0% conversion PRS”). Samples with the same PRS content for any PRS chemical conversion were termed polymer network isomers because they possess the same overall chemical composition but differ in molecular arrangement of network building blocks. For additional comparison, PPODA-free samples (blank samples) were also prepared by curing stoichiometric blends of DGEBA and DETDA. All blends were well mixed and degassed with a centrifugal mixer. They were then oven-cured at 80 °C for 24 hours and post-cured at 160 °C for 4 hours.
Figure 5.2. (a) FTIR spectra, epoxy-amine reactions of PRS (DGEBA+PPODA) at 80°C. (b) Reaction fractional conversion based on epoxide consumption.
5.2.3. Molecular Dynamics Simulations

MD systems of mixtures of DGEBA, PPODA, and DETDA were modeled using the generalized Amber force field\textsuperscript{20, 21} and simulated using LAMMPS\textsuperscript{22}. Crosslinked systems were generated using the capture-radius approach previously utilized\textsuperscript{23, 24}. $T_g$’s were measured with a temperature ramp between 145 K and 700 K at a ramp rate of 15 K/2ns. All observables were measured as averages of three replicas.

5.2.4. Uniaxial Compression

Once the samples were cured, they were cut into 6-by-6 cm rectangular sheets of 1 mm thickness. The sheets were then core-drilled to get disc-shaped samples of 8 mm in diameter and 1 mm in thickness. The error-bars associated with each of the data-points in the compression results were measured from at least six replicates (six identical specimens).

A servo-hydraulic INSTRON machine was used to perform the uniaxial compression test on the resulting thermosets under quasi-static strain rates. To get consistent results, the crosshead speed was set to 0.03 mm/s. The gauge section is demonstrated in Figure 5.3(a).
To study the rate dependent mechanical behavior of the polymer isomers, the similar disc-shape specimens were tested at high strain rates using a Kolsky bar in direct impact mode, as shown in Figure 5.3(b). The quasi-static strain rate was about 0.05 1/s, whereas the high strain rate was measured to be around 2000 1/s. There were two limitations for this study. The INSTRON apparatus (or similar facilities) are not capable of running beyond 1/s strain rates. Alternately, Kolsky bars in UDCCM facilities could not provide any strain rates under 500 1/s. Additionally, the momentum of the striker bar was never enough to provide stress-strain information beyond elastic limit. Hence, we only reported and compared the small-strain mechanical properties i.e. compressive modulus and yield strength.
Figure 5.3. (a) Gauge section of the INSTRON Machine for quasi-static compression test, (b) Kolsky bar set-up in Direct-Impact mode for high strain rate compression test.
5.3. Results and Discussion

5.3.1. Fracture Toughness

Once blank, control and modified samples were cured, they were cut into a compact tension specimen geometry. Compact tension testing was conducted under quasi-static tensile loading with crosshead speed of 1 mm/min following ASTM D5045.

The values of the critical stress intensity factor, $K_{ic}$, and the strain energy release rate, $G_{ic}$, were measured according to the theory of linear elastic fracture mechanics (LEFM). The $G_{ic}$ values are shown in Figure 5.4. A clear increase in fracture energy was observed for the PRS-modified systems. Since the composition and degree of cure for the control and modified samples were the same, it can be concluded that the network isomerization state substantially influences fracture behavior. Also, by looking at the results at the same PRS loading, it was observed that the degree of toughening is directly proportional to the chemical conversion of the embedded PRS.

The same trend was observed in the three batches with different PRS contents. The observed enhancement in toughness is significant because toughening was achieved not by incorporating the second phase (soft matter or nanoparticle), but
by means of rearranging the network structure. The results indicate that adding an additional processing step, i.e. the pre-reaction of some of the components, increased the fracture toughness of the material by well over 100%. This can be clearly observed by comparing the 0% conversion PRS to the corresponding 80% conversion PRS isomers.
Figure 5.4. Strain energy release rate, $G_{1c}$. 
5.3.2. Fracture Interface Nanostructure

Figure 5.5 contains representative SEM micrographs of the series of samples containing 10% PRS that show significant differences in fracture surface morphology. Comparing the fracture surfaces of blank and control samples in Figures 5.5(a) and 5.5(b), respectively, shows that the surface morphologies are rather similar and vary only in roughness. However, comparing the surface morphology of the polymer network isomers shown in Figures 5.5(b), 5.5(c), 5.5(d), and 5.5(e) reveals the presence of cavities on the fracture surfaces of modified samples shown in Figures 5.5(c), 5.5(d), and 5.5(e) and the absence of cavities on the surface of the control shown in Figure 5.5(b). The cavities on the fracture surfaces may explain why the modified systems possess much higher fracture toughness. It should be noted that no indication of macroscopic phase separation existed, since all blank, control, and modified samples were transparent to visible light as shown by the inset pictures on the top right hand corner of each micrograph in Figure 5.5.
Figure 5.5. SEM images of the fracture surfaces of the polymer network isomers. Surface morphology of the (a) blank samples, (b) control sample (0% conv. PRS), (c) PRS-modified sample (60% conv. PRS), (d) PRS-modified sample (70% conv. PRS), and (e) PRS-modified sample (80% conv. PRS). The control and modified samples are at 10% PRS content. The scale bars are 1 µm.
The average size of the cavities on the fracture surfaces was measured using the NIH image processing toolbox, “ImageJ”. Table 5.1 contains estimates of void diameters for modified samples. The average void diameter for the relatively circular features is roughly 30-45 nm. It was observed that the average void diameter of the 80% modified systems is slightly higher than the other modified systems even though the error bars are overlapping.
Table 5.1. Void diameter of the structural features (cavities) measured by ImageJ.

<table>
<thead>
<tr>
<th>Void Diameter (nm)</th>
<th>PRS Conversion</th>
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<tbody>
<tr>
<td></td>
<td>0%</td>
</tr>
<tr>
<td><strong>PRS Content</strong></td>
<td></td>
</tr>
<tr>
<td>10%</td>
<td>N/A</td>
</tr>
<tr>
<td>15%</td>
<td>N/A</td>
</tr>
<tr>
<td>20%</td>
<td>N/A</td>
</tr>
</tbody>
</table>
Small Angle X-ray Scattering was used to characterize the polymer samples prior to mechanical deformation. A SAXS/WAXS apparatus (Rigaku S-MAX 3000) was utilized for this purpose. Specimens were cut into thin disc-shaped geometries and polished. Each sample was irradiated with an X-ray having a wavelength of 1.54 Å (Cu Kα), and the scattered beam was collected with a 2D X-ray detector. Figure 5.6 shows scattered intensity (integrated over the azimuthal angle, χ) versus reciprocal space q-vector.

Figure 5.6 represents the scattered intensity of the control samples at different PRS (PPODA) contents, whereas Figure 5.7 plots the identical quantities of the polymer network isomers at 20% PRS loading. A scattering peak is observed at q = 0.049 Å⁻¹ in Figure 5.6 suggesting that the use of PPODA results in the formation of heterogeneous domains. According to Bragg’s law,²⁵,²⁶ this q-value corresponds to a d-spacing of about 13 nm. Increasing PRS (PPODA) content enhances the scattered intensity by increasing the concentration of the scatterers, which appears as an increase in the peak area. Partially reacting the PPODA shifts the peak to smaller q-values as shown in Figure 5.7, suggesting that the heterogeneous domains become larger with increasing PRS conversion. The calculated d-spacing values for each of the samples are listed in Table 5.2.
Figure 5.6. Scattered X-ray intensity vs. reciprocal space vector, q, for the “Control samples”.

Figure 5.7. Scattered X-ray intensity vs. reciprocal space vector, $q$, for the “Modified samples”.
Table 5.2. d-spacing of the heterogeneous domains for each of the samples in this study.

<table>
<thead>
<tr>
<th>PRS Content</th>
<th>d-spacing (nm)</th>
<th>0%</th>
<th>60%</th>
<th>70%</th>
<th>80%</th>
</tr>
</thead>
<tbody>
<tr>
<td>0%</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>10%</td>
<td>13.1</td>
<td>19.6</td>
<td>23.4</td>
<td>23.4</td>
<td></td>
</tr>
<tr>
<td>15%</td>
<td>13.4</td>
<td>18.0</td>
<td>21.5</td>
<td>25.4</td>
<td></td>
</tr>
<tr>
<td>20%</td>
<td>13.0</td>
<td>18.4</td>
<td>21.2</td>
<td>25.0</td>
<td></td>
</tr>
<tr>
<td>30%</td>
<td>12.6</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>40%</td>
<td>11.3</td>
<td>-</td>
<td>-</td>
<td>-</td>
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</tr>
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</table>
Table 5.2 shows that the concentration of PRS has little effect on the size of nano-domains. However, the size of the structural features is directly proportional to PRS conversion. Thus, according to the results in Table 5.2, the PRS technique creates larger but less dispersed structural features throughout the polymer network as PRS conversion increases. A general schematic of molecular network structure that illustrates this behavior is given in Figure 5.8. This Figure demonstrates that PPODA containing domains are smaller but more dispersed in control structures, and become larger and more coalesced (less dispersed) in modified structures.
Figure 5.8. Probable structural formation of the polymer network isomers. (upper) Control systems (dispersion of isolated PPODAs). (lower) PRS-modified systems (Coalesced PPODAs).
5.3.3. Fracture Mechanism

In highly-crosslinked epoxy polymers, there is little evidence of crazing; instead, considerable evidence of plastic shear deformation is observed.\textsuperscript{27, 28} In PRS modified systems considerable evidence of cavitation is found. It appears that the PRS-modified polymer networks behave like rubber-toughened epoxies in which energy dissipation occurs via cavitation (void formation) in the heterogeneous soft micro domains aided by plastic shear yielding around the particles,\textsuperscript{27, 29} even though the observed cavities for PRS systems are much smaller nano-cavities. Cavitation with plastic shear yielding, substantially promotes fracture energy. Larger void growth enhances toughness, and larger PRS domains promote the formation of larger cavities, as is the case for 80\% PRS-modified systems (Table 5.1) resulting in greater toughness improvements (Figure 5.4). Since the soft PRS domains are covalently bound parts of the polymer network, interface debonding commonly found in other toughening systems methods does not occur. This is clearly shown by the uniquely ragged edges of the voids on the fracture surfaces. SEM micrographs clearly show cavitation and enhanced plastic shear-yielding. The extent of the cavitation can be inferred by comparing the d-spacing obtained by SAXS given in Table 5.2 to the void sized measured using image analysis in Table
5.1. This concept along with the measured sizes (heterogeneous domains/voids) is demonstrated in Figure 5.9.
Figure 5.9. Schematic representation of nano-cavitation and shear-yielding in the plastic zone at the control and PRS-modified systems.
The cold-fractured surface morphology of a PRS-modified sample broken in LN$_2$ was compared to the surface morphology of the same material fractured at room temperature (RT). The corresponding micrographs are shown in Figure 5.10. Qualitatively, it appears that void formation is reduced in cold temperatures. The quantitative measurement of void surface coverage and void size were 0.3% and 37.4 ± 8.9 nm respectively for the cold-fractured system, whereas these measurements were significantly higher, roughly 1.7% surface coverage and 45.7 ± 15.7 nm, for the RT-fractured systems. The significant difference in void size and surface coverage between RT-fractured and cold-fractured surfaces provides further evidence that the cavitation mechanism is the dominant micromechanism in toughening of these polymer networks. However, in colder environments, or similarly at higher strain rates, the cavitation mechanism is moderated and therefore voids are smaller and less observable. Nevertheless, cavitation is still visible in cold fractured systems which suggests that this toughening mechanism is uncharacteristically activated even in extremely cold environments or analogously at high strain rates. This behavior could enable a new generation of epoxy systems used for adhesives and composites that endure extreme dynamic environments.
Figure 5.10. Room-temperature fractured (upper) vs. cold fractured (lower) surface morphology of an 80% PRS-modified sample, at 10% PRS content. The scale bars are 1 µm.
5.3.4. Glass Transition Temperature

The glass transition temperature for the polymer networks being investigated was measured using a TA-Q800 dynamic mechanical analyzer in single cantilever mode. DMA specimens were heated at a ramp rate of 2 °C/min under cyclic loading with a frequency of 1 Hz and amplitude of 15 μm. $T_g$ values were obtained from the peak position of the tan δ curves. It is interesting to note that the $T_g$ values were not the same for the system isomers. In fact, the PRS-modified systems revealed higher $T_g$ values compared to the corresponding control systems. Figure 5.11 shows the tan δ curves of the blank, control, and modified samples at 10% PRS content. It was observed that the $T_g$ values of the control systems follow the linear trend as predicted by Fox. However, the $T_g$ values of the PRS-modified systems deviate from the linear fit (Fox model) beyond 60% PRS conversions. These striking results are shown in Figure 5.12 where many formulations show $T_g$ well above the Fox model predictions.
Figure 5.11. Tan δ curves of the blank, control and modified samples at 10% PRS content.
Figure 5.12. Glass transition temperature of the control and modified samples at different PRS loading. The dashed line represents the Fox model.
One explanation for the elevated $T_g$ in the modified systems compared to the corresponding control systems could be the dispersion of PPODA molecules within the networks. When relatively dilute, each PPODA monomer is likely surrounded by DEDTA and DEGBA, but when coalesced into PRS regions, each PPODA monomer is likely surrounded by other PPODA monomers. As PPODA has a flexible backbone, it likely enhances the mobility of its neighbors in the network. Dilute PPODA enhances the mobility of more DEDTA than does coalesced PPODA, thereby degrading $T_g$ relative to pure DEDTA/DEGBA networks in the former case much more than in the latter. This is consistent with the observation that the control systems in which PPODA is dilute reveal lower glass transition temperatures than the corresponding modified systems.

5.3.5. Atomistic Molecular Dynamic Simulation

The structural formation of control and PRS-modified systems were modelled using atomistic molecular dynamic (MD) simulations. Mixtures of the two diamines, PPODA and DETDA, were used together with DGEBA, to compare the two blending protocols at constant overall DGEBA/DETDA/PPODA 2:1 amine:epoxy stoichiometry. The control involves curing DGEBA with both DETDA and PPODA, and the modified involves first partially curing DGEBA with PPODA and then adding DETDA and DGEBA to continue to a fully cured sample.
In this study, the 15 wt% PRS at 0% and 80% partial cure was modeled, and they labelled “control” and “modified”, respectively.

The glass transition temperatures from control and modified systems were obtained from a specific volume versus temperature curve by averaging over three independent replicas per system as shown in Figure 5.13. Predicted T_g was 410 K for the control systems and 425 K for the modified systems. This trend agrees with the results of the experiments. Possibly, this difference in T_g is a result of greater molecular flexibility in the control systems compared with the PRS-modified systems.
Figure 5.13. Specific Volume vs. Temperature for the control (0% conv. PRS) and modified (80% conv. PRS) systems, at 15% PRS content. Glass transition temperature is around 410 K for the control, and 425 K for the modified systems.
To test this hypothesis, we measured the root-mean squared fluctuation (RMSF) of the DETDA center of mass in the crosslinked systems as a function of temperature (Figure 5.14). The RMSFs clearly show that the DETDA rings fluctuate more in the control sample than in the PRS samples, at all temperatures. This results in lower molecular flexibility in the PRS-modified samples and consequently higher $T_g$'s relative to the control samples. The higher molecular flexibility and lower $T_g$ of control samples stems from the dilution of PPODA molecules. In the control samples, PPODA is well-dispersed, leading to a higher likelihood of DETDA/PPODA nonbonded contacts in the control vs. the PRS samples.
Figure 5.14. Root-mean squared fluctuation in the center-of-mass of DETDA rings vs. temperature for the control (0% conv. PRS) and modified systems (80% conv. PRS) at 15% PRS content.
5.3.6. Quasi-Static Mechanical Properties

So far, it has been shown that the modified samples are tougher and have more elevated glass transition temperatures than the corresponding control samples. Earlier, coarse-grained molecular simulations,\textsuperscript{15, 16} atomistic simulations,\textsuperscript{23} and experiments,\textsuperscript{17} were used to show that topology-based toughening does not sacrifice mechanical strength or material stiffness. To test this theory on the network isomers considered in this study, quasi-static mechanical testing was performed in uniaxial extension mode using the servo-hydraulic INSTRON apparatus.

At least 8 dog-bone shaped tensile coupons were produced, and the stress-strain curves were collected from at least six samples in each batch. The results are presented in Table 5.3. Additionally, the representative stress-strain curves of the PRS-modified samples and the corresponding control samples (at 10% PRS loading) are shown in Figure 5.15. It was found that increasing PRS content generally increases failure strain and reduces Young’s modulus and tensile strength. However, the data show that these properties do not vary appreciably within sets of isomers. This is particularly clear at 10% PRS content.
Figure 5.15. Representative stress-strain curves under mechanical extension for the PRS-modified (red) and Control samples at 10% PRS loading.
Table 5.3. Mechanical properties. Young’s modulus, Tensile strength, and Failure strain values.

<table>
<thead>
<tr>
<th>PRS Content</th>
<th>Young’s Modulus, E (GPa)</th>
<th>Tensile Strength, $\sigma_y$ (MPa)</th>
<th>Failure Strain, $\epsilon_r$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PRS Conversion</td>
<td>PRS Conversion</td>
<td>PRS Conversion</td>
</tr>
<tr>
<td>0%</td>
<td>2.7 ± 0.4</td>
<td>64.0 ± 14.7</td>
<td>5.3 ± 0.8</td>
</tr>
<tr>
<td>10%</td>
<td>2.0 ± 0.1</td>
<td>2.2 ± 0.1</td>
<td>2.1 ± 0.1</td>
</tr>
<tr>
<td>15%</td>
<td>2.1 ± 0.1</td>
<td>2.1 ± 0.2</td>
<td>1.7 ± 0.2</td>
</tr>
<tr>
<td>20%</td>
<td>1.8 ± 0.1</td>
<td>1.6 ± 0.1</td>
<td>1.5 ± 0.1</td>
</tr>
</tbody>
</table>
5.3.7. Effect of Chain Length

Thus far the effect of PRS content and PRS chemical conversion on mechanical performance and glass transition temperature has been explored. However, the effect of chain length or the molecular weight of the flexible curative, Jeffamine, was not investigated.

To understand the effect of the molecular weight of the flexible curing agent, similar samples were prepared, as discussed earlier, except the PRS were made from Jeffamine D-2000. Using Jeffamine D-2000 instead of Jeffamine D-4000 in formulation creates nano-structures, similar to the ones formed in the Jeffamine D-4000 samples, except crosslinking density of the heterogeneous domains are higher.

Here we examine the effect of PRS chemical conversion on fracture behavior and glass transition temperature of the modified systems. The chemical compounds, processing, and curing protocol were exactly the same as the systems with Jeffamine D-4000, except PRS chemical conversion for the Jeffamine D-2000 was selected at 0%, 50%, and 60%, respectively. Combined FTIR-rheology experiments revealed delay in gelation (than the theoretical limits), for the systems that were composed of curing agents with relatively large AHEW, such as the PRS made from Jeffamine D-4000. The plots of coupled viscosity - reaction conversion versus
reaction time are shown in Appendix H. This phenomena was due to the formation of cyclic chains as well as the steric hindrance effect due to existence of non-reactive backbone of the Jeffamine molecules. In the limiting case, when AHEW is very large, the system never forms a crosslinked structure. This concept scrutinized in section 7.3.6.

Figure 5.16 shows the average strain energy release rates for the stoichiometric blends of DGEBA (EPON 825) and DETDA reinforced with PRS made from DGEBA and Jeffamine D-2000. A moderate increase in fracture energy for the PRS-modified systems with 50% and 60% PRS conversion was noticed when comparing the polymer network isomers at some fixed PRS weight percent, though the toughness enhancement was not as high as the system isomers composed of Jeffamine D-4000.
Figure 5.16. Strain energy release rate, $G_{ic}$, for the systems reinforced with PRS made from Jeffamine D-2000.
To investigate glass transition temperature of the polymer network isomers, dynamic mechanical analysis was conducted on the samples in single cantilever mode, consistent with DMA characterization on the system isomers with Jeffamine D-4000. Figure 5.17 shows the peak position of tan δ curves vs. temperature for each individual systems. Similar to the systems made from Jeffamine D-4000, $T_g$ values start to deviate from the linear fit (Fox model), and the deviation is observed to be proportional with the PRS chemical conversion. The improved $T_g$ can be justified with the same concept as discussed for the Jeffamine D-4000.

When relatively dilute, each PPODA monomer (Jeffamine D-2000 here) is likely surrounded by DEDTA and DEGBA, but when coalesced into PRS regions, each PPODA monomer is likely surrounded by other PPODA monomers. As PPODA has a flexible backbone, it likely enhances the mobility of its neighbors in the network. Dilute PPODA enhances the mobility of more DEDTA than does coalesced PPODA, thereby degrading $T_g$ relative to pure DEDTA/DEGBA networks in the former case much more than in the latter. This is consistent with the observation that the control systems in which PPODA is dilute reveal lower glass transition temperatures than the corresponding modified systems.
Figure 5.17. Tan δ curves of the blank, control and modified samples at 15% PRS content.
Figure 5.18. Glass transition temperature of the control and modified samples at different PRS loading. The dashed line represents the Fox model.
5.3.8. Time Temperature Superposition (TTS)

One thought on the elevated glass transition is due to presence of a secondary transition between $\alpha$ and $\beta$ transitions. In other words, existence of a transition between $\alpha$ and $\beta$ could cause a delay in the appearance of $\alpha$ transition at a fixed temperature ramp, thus showing the glass transition temperature of the PRS-modified samples at slightly higher $T_g$. To test this hypothesis, we measured the energy required for a given system to enter the rubbery state from glassy state using Time Temperature Superposition (TTS). Presence of any secondary transition, even a weak one, reduces the amount of energy required to activate the segmental motion necessary to enter the rubbery state.

As discussed in the background, the TTS principle states that time and temperature are identical to the extent that data at one temperature can be superimposed on data at another temperature by shifting the curves along the time axis.\textsuperscript{31} The activation energy required for a system to pass a transition state can be measured by the Arrhenius equation as following:

$$
\log a_T = \frac{E_a}{R} \left( \frac{1}{T} - \frac{1}{T_r} \right)
$$

(5.1)
TTS specimens were tested with a Dynamic Mechanical Analyzer in single cantilever mode. Rectangular samples (2 x 12 x 35 mm) were prepared. The samples were heating in a stepwise heating protocol in a temperature range of 100 °C to 220 °C with an increment of 5 °C and 5 min soak time. When samples equilibrated at each specified temperature, material properties were collected under a frequency sweep in a frequency range of 0.1 Hz to 100 Hz (log scale) with 4 points per decade. The T<sub>g</sub> of each sample was chosen as the reference temperature, and the temperature range was selected such that sufficient data below and above T<sub>g</sub> could be collected.

The tan δ master curves versus frequency are shown in the Figures 5.19 and 5.20. It is easily observed that the tan δ curves are almost identical for the polymer network isomers, and the degree of crosslinking of the PRS is not significantly affecting the area or breadth of tan δ.
Figure 5.19. Superimposed master-curves of tan δ vs. frequency for the polymer network isomers at 10% PRS content.
Figure 5.20. Superimposed master-curves of tan δ vs. frequency for the polymer networks at 0% PRS conversion (control systems).
While the tan δ vs. frequency graphs look identical (Figure 5.19), the tan δ graphs of the control samples at various PRS content represent a reduction in peak area as PRS content goes up (Figure 5.20).

Accordingly, the activation energy of the α-transition was measured for each of the systems based on the equation (5.1). The values of $E_a$ are shown in Figures 5.21 and 5.22 for the PRS made from Jeffamine D-4000 and Jeffamine D-2000, respectively.
Figure 5.21. Activation energy of $\alpha$-transition for the systems with the PRS made from Jeffamine D-4000.
Figure 5.22. Activation energy of α-transition for the systems with the PRS made from Jeffamine D-2000.
According to the results shown in Figures 5.21 and 5.22, it can be concluded that the presence of the flexible curing agents, PPODAs, significantly reduces the amount of energy required to activate the segmental motion necessary to bring the polymer from the glassy state to the rubbery state. This energy decreases with increasing PPODA content. However, the major finding implies that this activation energy is almost invariant for the polymer isomers at constant PRS contents for both PRS systems (Jeffamine D-2000, and Jeffamine D-4000). This observation was important because it provided necessary information to declare that the deviation and enhancement of $T_g$ from linear Fox model for the PRS-modified systems is not due to any secondary transition between $\alpha$ and $\beta$, and it is solely due to the arrangement and molecular structure of the polymer network.

5.3.9. Swelling Study

In a separate study, the swelling capacity of the resulting samples was investigated. Prepared specimens from each category were soaked in tetrahydrofuran at room temperature for a period of time adequate to achieve equilibrium swollen state. Figure 5.23 represents the equilibrium solvent mass uptake for the systems investigated here.
Figure 5.23. Relative solvent mass uptake for the polymer systems investigated in this study.
Equilibrium swelling results indicated that the swelling capacity (equilibrium mass uptake) increased with the increase of the PPODA contents. However, at constant PRS loading, the difference in mass uptake was not substantial between polymer network isomers. This indicates that the induced structural variations as a result of the PRS degree of conversion does not change the average overall molecular packing (crosslinking density), even though the local molecular packing are different.

5.3.10. Rate Dependent Mechanical Behavior under Compression

Stress-time curves under high strain rates compressive loading were collected using Kolsky bars as described previously. Figure 5.24 and 5.25 are the representative stress-time curves for the control and modified systems, respectively. Additionally, the respective stress-strain curves for the same samples under quasi-static rates compressive loading are shown in Figures 5.26 and 5.27.
Figure 5.24. Representative stress-time curves under high strain rates compressive loading for the control samples (0% conversion PRS) at different contents of PRS.
Figure 5.25. Representative stress-time curves under high strain rates compressive loading for the modified samples (80% conversion PRS) at different contents of PRS.
Figure 5.26. Representative stress-strain curves under quasi-static strain rates compressive loading for the control samples (0% conversion PRS) at different contents of PRS.
Figure 5.27. Representative stress-strain curves under quasi-static strain rates compressive loading for the modified samples (80% conversion PRS) at different contents of PRS.
Accordingly, Figures 5.28 and 5.29 show the average values of Young’s modulus for each of the synthesized polymer networks under quasi-static strain rates and high strain rates, respectively. The error bars associated with each data point are measured from at least 6 replicates. Results clearly imply that increasing the Jeffamine content decreases the elastic modulus for both quasi-static strain rates and high strain rates.
Figure 5.28. Compressive elastic modulus under quasi-static strain rates of the thermosets tested in this study.
Figure 5.29. Compressive elastic modulus under high strain rate of the thermosets tested in this study.
According to the results, the quasi-static strain rate compressive modulus was not preserved for the polymer network isomers. In fact, at a specific PRS content, compressive modulus decreased with the increase of the PRS conversion. In contrast, high strain rate compressive modulus increased with the increase of the PRS conversion excepting the batches with 10% PRS content. The high strain rate compressive modulus increase could be due to the presence of the heterogeneities that were incorporated into the crosslinked structure. A possible explanation for this observation is that, under quasi-static strain rate compression, the size effect dominates the dispersion effect, and thus control systems (where heterogeneous domains are less coalesced but more dispersed) reveal higher moduli than the PRS-modified systems (where the heterogeneities are larger and more coalesced). However, under high strain rate compression, the dispersion effect dominates the size effect thereby making the PRS-modified systems look stiffer than the control systems. In other words, the time scale in this experiment is short and heterogeneities do not have sufficient time to respond to the applied compressive load. The noticeable enhancement in compressive modulus could offer the application of the PRS-modified polymer networks in extreme dynamic environments, such as anti-corrosive and bulletproof coatings.

Similar to the trend for compressive modulus, quasi-static rate yield strength was observed to decrease with the increase of Jeffamine content in the crosslinked
structures. However, high strain rate yield strength was almost invariant with increasing Jeffamine content. In addition, comparing the quasi-static rate yield strength of the isomers (control and PRS-modified systems) at the same PRS content, either little to no reduction was observed. In contrast, when comparing the high strain rate yield strength of the control and PRS-modified systems, there is a significant increase of this quantity for the isomeric systems at 15% PRS content and above. It is believed that the observed increase of the yield stress is due to secondary molecular processes. A similar increase in yield stress was observed when the polymer networks were tested in cold environments, close enough to the secondary relaxation temperature, $T_\beta$. The increase of strain rate, which is analogous to the decrease of temperature, would make the polymer chains stiffer by reducing the molecular mobility of the polymer chains, thus making the polymer networks more resilient by absorbing more storage energy. The average yield strength for system isomers under quasi-static and high strain rates are shown in Figures 5.30 and 5.31.
Figure 5.30. Compressive yield strength under quasi-static strain rates of the thermosets tested in this study.
Figure 5.31. Compressive yield strength under high strain rates of the thermosets tested in this study.
In addition to the compression tests, SAXS was conducted on the disc-shape specimens before and after quasi-static compression using a Rigaku SAXS apparatus in the centralized research facilities at Drexel University. The specimens before compression were labelled as “relaxed” samples. These samples were deformed under a uniaxial compressive loading (using an INSTRON apparatus) up to certain strain values of about 30%. The resulting specimens were labelled as “compressed” samples.

For some of the samples, Small Angle X-ray Scattering (SAXS) was conducted before and after compression test. These results are shown in the Figure 5.32. It was shown that the peak positions do not significantly shift to lower or higher q values, meaning that the size of the heterogeneities are essentially invariant during compression, even though their shapes might vary.
Figure 5.32. SAXS results of the polymer networks before (green curve) and after (black curve) compression. (a) Blank sample, (b) Control sample (0% conv. PRS), (c) PRS-modified (70% conv. PRS) and (d) PRS-modified (80% conv. PRS).
5.3.11. Effect of the Molecular Weight of the Aliphatic Curing Agents on Cure Kinetics of Epoxy-Amine Reactions

As discussed, the extent of the epoxy-amine curing reactions were accurately measured using FTIR in nearIR region. However, the reactivity ratio of the functional groups “substitution effect” has not been investigated. It is well-known from literature that the ratio of primary amine (NH$_2$) reactivity to the secondary amine reactivity (NH) (also known as the “substitution factor”) is critical in determining the structural topology during reactions.$^{19,33}$

Some kinetic models assume that the reactivity of primary amines and secondary amines are the same. Since primary amines have two reactive hydrogen atoms, equal reactivity essentially yields $k_2/k_1 = 0.5$. However, in reality the reactivity of primary amine is higher than that of the secondary amine resulting lower substitution factors (< 0.5)$^{34-36}$

For the systems examined here, it is important to consider the effect of substitution factor on structural topology. Considering that both $k_1$ and $k_2$ as the reaction rate constants show Arrhenius dependence to temperature:
\[ k_1 = A_1 \exp\left(\frac{-E_{a,1}}{RT}\right) \]  

(5.2)

\[ k_2 = A_2 \exp\left(\frac{-E_{a,2}}{RT}\right) \]  

(5.3)

Therefore,

\[ \frac{k_2}{k_1} = \frac{A_2}{A_1} \exp\left(\frac{E_{a,1} - E_{a,2}}{RT}\right) \]  

(5.4)

where \( A_1 \) and \( A_2 \) are the pre-exponential factors, and \( E_{a,1} \) and \( E_{a,2} \) are the corresponding activation energies, respectively.

Equation 5.4 shows the dependence of the substitution factor, and subsequently network topology, to temperature. Hence, to eliminate the effect of temperature on network topology, polymer system isomers were cured (and post-cured) at the same curing conditions.

We have conducted in-situ FTIR spectroscopy to investigate the substitution effect of the aliphatic curing agents, polyetheramines (PEAs), with different chain lengths when reacting with the DGEBA at the same curing temperature of 80 °C. Accordingly, blends of stoichiometric amounts of DGEBA and PEAs with molecular weights of 230, 400, 2000, and 4000 g/mol were prepared. These systems
were labelled as DGEBA-PEA$_{230}$, DGEBA-PEA$_{400}$, DGEBA-PEA$_{2000}$, and DGEBA-PEA$_{4000}$, respectively.

A NearIR spectrometer Nexus 870 (Thermo Nicolet Corp.) with CaF$_2$ beam splitter was employed for this purpose. Capillary glass tubes (ID = 1.6 + 0.05 mm) were used to hold the samples. The nIR spectra were collected at a resolution of 4 cm$^{-1}$ in absorbance mode. The resulting spectra at each time was measured from the average of 32 individual scans. The peaks of interest were the epoxy peak at 4530 cm$^{-1}$, the primary amine peak at 4925 cm$^{-1}$, and the primary/secondary amine peak at 6510 cm$^{-1}$.

Considering the reaction mechanism, the extent of epoxy-amine reactions in terms of epoxy group ($\alpha$) and N-H bands ($\beta$) from the peak area of the oxirane rings and N-H groups in absorption mode is defined as

$$
\alpha_e = \frac{A_e(0) - A_e(t)}{A_e(0)} \quad (5.5)
$$

$$
\beta_{N-H} = \frac{A_{N-H}(0) - A_{N-H}(t)}{A_{N-H}(0)} \quad (5.6)
$$

where “A” is the absorbance peak area and subscripts “e” and “N-H” represent the epoxy and amine, at “0” initial and “t” time t.
It is well-known that the epoxy-amine curing reaction are autocatalytic, which means that presence of OH group in the reaction (either coming to the reaction mixture as an impurity or forming during epoxy ring opening mechanisms) catalyzes the reaction.\textsuperscript{38-40} Two kinetic schemes are generally considered for modeling the epoxy-amine reactions. A non-catalyzed and an auto-catalyzed.

The auto-catalyzed pathway was considered for the numerical investigations, since the non-catalyzed path poorly describes the reaction phenomenon. Accordingly, the reaction paths are

\begin{equation}
[E] + [PA] + [OH] \overset{k_1}{\rightarrow} [SA] + 2[OH]
\end{equation}

\begin{equation}
[E] + [SA] + [OH] \overset{k_2}{\rightarrow} [TA] + 2[OH]
\end{equation}

where \([E],[PA],[SA],[TA] and [OH]\) are the molar concentrations of the epoxy, primary amine, secondary amine, tertiary amine, and the hydroxyl groups, respectively.

These concentrations at each stage of polymerization can be measured from the extents of reaction \(\alpha\) and \(\beta\), and mass balance equations as follows:
\[ [E] = [E]_0 (1 - \alpha) \]  \hspace{1cm} (5.9)

\[ [PA] = [PA]_0 (1 - \beta) \]  \hspace{1cm} (5.10)

\[ [SA] = [E]_0 (\beta B - \alpha) \]  \hspace{1cm} (5.11)

\[ [TA] = [E]_0 (\alpha - \beta \frac{B}{2}) \]  \hspace{1cm} (5.12)

\[ [OH] = [OH]_0 + [E]_0 - [E] \]  \hspace{1cm} (5.13)

Here, \( B = 2 \frac{[PA]_0}{[E]_0} \) is the initial concentration between primary amine and epoxy. The initial concentrations of epoxy and primary amine were measured from the initial weight of each of the components and the corresponding densities, according to their materials spec sheets. Moreover, the initial concentrations of secondary amine and tertiary amine were assumed zero. The initial concentration of OH was measured via trial/error. It was not possible to accurately measure the initial hydroxyl contents because of dissociation of a negligible amount of water molecules that are present in the mixtures.
The system of ordinary differential equations and the corresponding initial conditions were prepared as below:

\[
\frac{d[E]}{dt} = -k_1[E][PA][OH] - k_2[E][SA][OH] \tag{5.14}
\]

\[
\frac{d[PA]}{dt} = -k_1[E][PA][OH] \tag{5.15}
\]

\[
\frac{d[SA]}{dt} = k_1[E][PA][OH] - k_2[E][SA][OH] \tag{5.16}
\]

\[
\frac{d[TA]}{dt} = k_2[E][SA][OH] \tag{5.17}
\]

\[
\frac{d[OH]}{dt} = k_1[E][PA][OH] + k_2[E][SA][OH] \tag{5.18}
\]

The above system of nonlinear differential equations were solved using the non-stiff MATLAB ODE solver (ode45). A MATLAB routine was generated. The numerical concentrations were obtained by solving the set of differential equations for the values of \(k_1\) and \(k_2\) and the deviation of numerical epoxy and primary amine concentrations were calculated from the corresponding experimental values. Values of \(k_1\) and \(k_2\) were obtained and reported as the primary amine and
secondary amine rate constants from the set that shows the least deviation from experimental epoxy and primary amine concentrations. The MATLAB generated code is shown in Appendix D.

It is important to note that for all the systems the least square error only applied to experimental concentrations up to 0.58 extent of curing reactions. This value, 0.58, is the theoretical limit of gel point for the di-functional epoxy tetra-functional amine systems.\textsuperscript{41} Epoxy-amine reactions are kinetically-controlled at early stages of polymerization until the gel point. After gelation, diffusion limitation always affects the final stages of cure. Therefore, after a given level of conversion a deviation from the autocatalytic model is observed since the reactions are diffusion-controlled rather than kinetically-controlled.\textsuperscript{42-44}

The average values of \( k_1 \) and \( k_2 \) at 80 °C and the average substitution factors from three replicates for each system are shown in Figures 5.33 and 5.34. The individual values of \( k_1 \), \( k_2 \), and \( k_2/k_1 \) from each replicates are also listed in Table 5.4. In addition, the numerical and experimental concentrations for the blends are demonstrated in Figures 5.35, 5.36, 5.37, and 5.38.
Figure 5.33. Average values of primary amine-epoxy ($k_1$), secondary amine-epoxy ($k_2$) reaction rate constants at 80 °C, from at least three replicates for each system.
Figure 5.34. Average values of substitution factor at 80 °C, from at least three replicates per system.
Table 5.4. Primary amine ($k_1$) and secondary amine ($k_2$) rate constants at each individual run. Reaction temperature was at 80 °C. ($k_1$ and $k_2$ has the unit of $\text{lit}^2\cdot\text{mol}^{-2}\cdot\text{min}^{-1}$)

<table>
<thead>
<tr>
<th>Thermosetting system</th>
<th>1st trial</th>
<th>2nd trial</th>
<th>3rd trial</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$k_1$</td>
<td>$k_2$</td>
<td>$k_2/k_1$</td>
</tr>
<tr>
<td>DGEBA-PEA$_{230}$</td>
<td>0.0115</td>
<td>0.0034</td>
<td>0.2957</td>
</tr>
<tr>
<td>DGEBA-PEA$_{400}$</td>
<td>0.0110</td>
<td>0.0029</td>
<td>0.2636</td>
</tr>
<tr>
<td>DGEBA-PEA$_{2000}$</td>
<td>0.0127</td>
<td>0.0020</td>
<td>0.1575</td>
</tr>
<tr>
<td>DGEBA-PEA$_{4000}$</td>
<td>0.0227</td>
<td>0.0013</td>
<td>0.0573</td>
</tr>
</tbody>
</table>
Figure 5.35. Numerical (solid lines) and experimental (dots) concentration profiles of the reactive groups during the curing reactions of DGEBA-PEA$_{230}$ at 80 °C.
Figure 5.36. Numerical (solid lines) and experimental (dots) concentration profiles of the reactive groups during the curing reactions of DGEBA-PEA$_{400}$ at 80 °C.
Figure 5.37. Numerical (solid lines) and experimental (dots) concentration profiles of the reactive groups during the curing reactions of DGEBA-PEA\textsubscript{2000} at 80 °C.
Figure 5.38. Numerical (solid lines) and experimental (dots) concentration profiles of the reactive groups during the curing reactions of DGEBA-PEA$_{4000}$ at 80 °C.
As discussed, reactivity of primary amines is generally higher than reactivity of the secondary amines for all systems investigated here \((k_1 > k_2)\). However, as shown in Figure 5.34 and Table 5.4, the substitution factor showed a decreasing trend as the molecular weight of the curing agent, PEA, became larger.

One probable explanation is that nucleophilic character of the hydrogen atoms on primary amines are higher than nucleophilic character of the hydrogen atoms on secondary amines. Therefore, epoxy-primary amine ring opening reaction is faster than epoxy-secondary amine. This phenomena could explain why epoxy-primary amine reactions are faster than epoxy-secondary amine reactions, however, it cannot explain why substitution effect is reduced as the molecular weight of the curing agent gets larger.

The most probable explanation for this observation is the steric hindrance effect due to the addition of one epoxy to a primary amine. Even for smaller molecules such as PEA\textsubscript{230} and PEA\textsubscript{400}, this addition reactions causes \(k_2\) to be lower than \(k_1\), causing the substitution factor to be lower than the theoretical limit of 0.5. The same description is valid for explaining why substitution factor is decreasing with the increase of PEA molecular weight. In fact, when primary amines react with epoxides, the additional reactions of the forming secondary amines are hindered by the non-reactive backbone of the molecule, thus showing a lower \(k_2\) at the same
reaction conditions. Consequently, the larger the size of curing agents, the bulkier the non-reactive backbones, the smaller the reactivity of secondary amines will be.

5.4. Conclusion

A novel processing technique for toughening thermosets was introduced through which partially reacted substructures of a low-$T_g$ thermoset at different extents of polymerization were embedded into a high-$T_g$ majority-phase thermoset. It was shown that the PRS-modified samples are tougher than the corresponding controls, and the toughness is directly proportional to the chemical conversion of the embedded PRS. The 80% conversion PRS-modified samples were almost twice as tough as the corresponding control samples. SEM micrographs from fracture surfaces of the modified samples showed voids, whereas none were seen on the fracture surfaces of the control samples. This implies that the principal energy dissipating mechanism during fracture in the modified structures is cavitation with associated plastic shear yielding. SAXS results represented the existence of heterogeneous domains of about 12-25 nm. The domain size increased with increasing of PRS conversion, indicating that the PRS technique led the PPODAs to be more coalesced. Also observed, was that the glass transition temperatures of the modified systems were higher than those of the control systems. In addition, quasi-
static mechanical extension did not show substantial differences in mechanical strength and modulus between system isomers. Overall, polymer network isomers with improved thermal and mechanical properties were developed by rearranging the molecular structures through an additional step in the processing of these polymers. This further supports the idea that the network isomerization state can be tuned to produce materials with improved toughness and glass transition temperature without sacrificing essential mechanical properties such as strength and stiffness. The results on the epoxy-amine system investigated herein can be directly and economically applied to current industrial coating, adhesive, and composite formulations. Although topology-based toughening was investigated on crosslinked epoxy-amine polymers, the concept should be applicable to all thermoset chemistries and perhaps to other brittle network forming materials.

5.5. List of References


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41. Flory, P. J. Journal of the American Chemical Society 1941, 63, (11), 3083-3090.


Chapter 6. Investigating the Effect of $T_g$ on Mechanical Properties of Epoxy-Amine Polymer Networks with Altered Topology

6.1. Introduction

Chapter 3 revealed significant ductility for a crosslinked polymer in glassy state upon uniaxial tensile deformation, and that the observed energy absorption is due to local molecular motions and plastic void growth of the distinct topological structures in the form of molecular surfaces (protovoids) that were embedded in polymer networks. Next, as discussed in Chapter 5, polymer isomers were formulated with some distinct structural domains (PRS) throughout the network. The modified structures with larger PRS domains revealed higher toughness, about two-and-half times larger. However, these polymer isomers did not show significant plastic deformation similar to the characteristics observed earlier in the RES-modified samples, discussed in Chapter 3.

The lack of ductility in the PRS-modified systems could be due to two reasons: (1) relatively large difference between $T_g$ of the PRS-modified samples and testing temperature (room temperature), or (2) absence of the molecular surfaces that could mimic the role of the potential voids in the RES-modified systems. The first
hypothesis was comprehensively investigated and explained in this Chapter, while the second is explored in the next Chapter.

Accordingly, effect of the final $T_g$ on the mechanical performance and stress-strain behavior of polymer networks will be discussed here. Three systems with various $T_g$ ranging from 60 °C – 180 °C were prepared. In addition, poly(propylene-oxide)diamines (PPODA) with various molecular weights reacted with monooepoxide phenyl glycidyl ether (PGE). The resulting non-reactive adducts, referred to as “capped PPODAs” (cPPODAs) were incorporated in the resin formulations to create the molecular surfaces (protovoids). In this study, capped PPODAs serve as solvent species as in Chapter 3, but they remain in polymer networks.

6.2. Experimental

6.2.1. Material

The difunctional epoxy resin used is Diglycidyl Ether of Bisphenol-A (DGEBA), EPON 825 with $n=0.07$, (Miller-Stephensen). Three diamine curing agents were used as the main curatives: (DETDA), EPIKURE W (Miller-Stephensen), and poly(propylene-oxide)diamine, PPODA, Jeffamine D-230 and D-400 (Huntsman).
In addition, poly(propylene-oxide)diamine, PPODA, Jeffamine D-2000 and D-4000 (Huntsman) were used as the curing agents for phenyl glycidyl ether, PGE, (Sigma-Aldrich) to formulate the capped PPODAs. These materials are shown in Figure 6.1.
Figure 6.1. Chemical structure of the resins used in this study. (a) Diglycidyl Ether of Bisphenol-A (DGEBA), (b) Phenyl Glycidyl Ether (PGE), (c) DiEthyl-Toluene-DiAmine (DETDA), (d) Poly(Propylene-Oxide)DiAmine (PPODA), x = 2.5, 6.1, 33, 68.
6.2.2. Processing

Three individual blends were prepared to form the non-reactive adducts, capped PPODAs. Accordingly, a stoichiometric amount of PGE – PPODA\(_{x=6.1}\), PGE – PPODA\(_{x=33}\), and PGE – PPODA\(_{x=68}\) were mixed and degassed in a Thinky mixer, and cured at 80 °C for about 72 hours. The FTIR spectra revealed the existence and ongoing epoxy-amine reactions in the curing conditions. Termination of curing reactions was indicated by the complete consumption of epoxy-primary amine reactive groups. Because PGE molecules have only one component, the only reaction pathway is the formation of a non-reactive product. Resulting adduct is referred to as “capped PPODA” in this Chapter and is shown in Figure 6.2.
Figure 6.2. Molecular structure of the inert “capped PPODAs”. The value of x can be varied depending on the PPODAs reacted with PGE. Average x = 6.1, 33, and 68 in this study.
Depending on the chain length of the capped PPODA, the viscosity of adducts were different. The capped PPODA$_{x=6.1}$ showed highest viscosity where the capped PPODA$_{x=68}$ exhibited the lowest, at room temperature. Viscosity of these systems is primarily determined by the intermolecular interactions. When smaller PPODAs are used, more PGE was required to maintain the stoichiometric ratio. Therefore, molar concentration of the aromatic rings (present in the molecular structure of PGEs) was higher in the structure of adducts in this case. The π-stacking interactions increase and result in higher viscosity at room temperature.

Aside from preparation of the capped PPODAs, three thermosetting systems with various $T_g$ were studied in this work. Stoichiometric amounts of DGEBA – DETDA, DGEBA – PPODA$_{x=2.5}$, and DGEBA – PPODA$_{x=6.1}$ were prepared. Then 5% by weight from each of the capped PPODAs was added to the blends. Additionally, blank samples were prepared by mixing the stoichiometric amount of each of the above systems. Resulting mixtures were oven-dried and cured at 80 °C for 12 hours followed by a post-curing step at 160 °C for 4 hours.
6.3. Results and Discussion

Figure 6.3 shows the dog-bone specimens after post-cure. The last row, which are the polymer networks with 5% capped PPODA\textsubscript{x=68}, revealed visible phase separation and were excluded from further characterization and analysis. The reason for phase separation could be due to the relatively large size of the incorporated capped PPODAs. The presence of such adducts create large domains that scatter visible light beams, thus causing the opaque look.
Figure 6.3. The dog-bone shape specimens for mechanical extension characterization. The thermosets with capped PPODA_{x=68}, specimens in the last row, are phase separated.
The probable structural formation of the polymer networks are shown in Figure 6.4. These systems are identical to the systems described in Chapter 3, yet the resulting samples cannot be called polymer isomers because compositions are different. If we could extract the capped PPODAs after cure, the resulting structures would have been called “polymer isomers”.
Figure 6.4. The illustration of probable network structure when cured with and without capped PPODAs. (a) Blank, (b) 5% capped $\text{PPODA}_{x=6.1}$, (c) 5% capped $\text{PPODA}_{x=33}$. 
From previous studies, it is comprehensively understood that the presence of a soft phase in polymer network structures reduces tensile strength, modulus, and glass transition temperature. However, in this study we aimed to explore if topological variations could affect stress-strain behavior for systems with various $T_g$’s, similar to the systems previously discussed in Chapter 3. Here, capped PPODAs perform the role of inert solvent species. During polymerization capped PPODAs are encapsulated by thermosets without any covalent bond formation in the directionality where the capped PPODAs are present. This results in the creation of molecular surfaces (protovoids), and subsequently variations in network topology. The effects of topology on behavioral characteristics of thermosetting systems in a broad range of $T_g$ is discussed herein.

6.3.1. Glass Transition Temperature

A dynamic mechanical analyzer, DMA TA-Q800 instrument was used to measure the viscoelastic properties. Single cantilever specimens (35x12x2 mm) were loaded under a cyclic loading with an amplitude of 15 µm and a frequency of 1 Hz. The viscoelastic properties were measured at a heating rate of 2 °C/min. The temperature range was varied depending on the type of thermoset that was analyzed.
$T_\text{g}$ values were measured from the position of the tan $\delta$ peak. Figure 6.5 shows a representative tan $\delta$ for the polymer networks composed of DGEBA and DETDA. As expected, and unlike the RES-modified systems, $T_\text{g}$ values were not the same here. The system with 5% inclusion of capped PPODA$_{x=33}$ exhibited the lowest $T_\text{g}$ and the highest peak breadth. A summary of peak analysis on tan $\delta$ vs. temperature curves is listed in Table 6.1.
Figure 6.5. Representative tan δ curves for the DGEBA-DETDA systems with varying capped PPODA contents.
Table 6.1. Summary of the DMA results, including $T_g$, tan $\delta$, FWHM, Flexural modulus at room temperature, and crosslinking density ($\nu$).

<table>
<thead>
<tr>
<th>Thermosetting system</th>
<th>$T_g$ ($^\circ$C)</th>
<th>Peak area</th>
<th>FWHM ($^\circ$C)</th>
<th>RT Flex. Modulus (GPa)</th>
<th>$\nu$ (mol/cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>DGEBA-DETDA</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Blank</td>
<td>197.3</td>
<td>8.0</td>
<td>21.9</td>
<td>2.41</td>
<td>0.0036</td>
</tr>
<tr>
<td>cPPODA$_{x=6.1}$</td>
<td>192.1</td>
<td>8.1</td>
<td>23.9</td>
<td>2.5</td>
<td>0.0033</td>
</tr>
<tr>
<td>cPPODA$_{x=33}$</td>
<td>181.4</td>
<td>8.05</td>
<td>27.6</td>
<td>2.68</td>
<td>0.0031</td>
</tr>
<tr>
<td><strong>DGEBA-PPODA$_{x=2.5}$</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Blank</td>
<td>101.2</td>
<td>6.0</td>
<td>10.6</td>
<td>2.73</td>
<td>0.0027</td>
</tr>
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<td>cPPODA$_{x=6.1}$</td>
<td>93.0</td>
<td>6.8</td>
<td>12.4</td>
<td>2.92</td>
<td>0.0023</td>
</tr>
<tr>
<td>cPPODA$_{x=33}$</td>
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<td>6.9</td>
<td>14.0</td>
<td>2.27</td>
<td>0.0021</td>
</tr>
<tr>
<td><strong>DGEBA-PPODA$_{x=6.1}$</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Blank</td>
<td>61.7</td>
<td>6.8</td>
<td>10.3</td>
<td>2.63</td>
<td>0.0023</td>
</tr>
<tr>
<td>cPPODA$_{x=6.1}$</td>
<td>57.6</td>
<td>7.7</td>
<td>11.2</td>
<td>2.45</td>
<td>0.0018</td>
</tr>
<tr>
<td>cPPODA$_{x=33}$</td>
<td>55.8</td>
<td>7.4</td>
<td>12.4</td>
<td>1.96</td>
<td>0.0016</td>
</tr>
</tbody>
</table>
According to the data provided in Table 6.1, in all the systems studied, Full-Width-Half-Maximum (FWHM) increased where crosslinking density decreased as the size of the capped PPODA grew. The results implied that, for fully cured thermosets, inter-molecular packing reduced and polymer networks became less homogenous when larger capped PPODAs are incorporated.

6.3.2. Mechanical Properties

The principle objective of this study was to investigate the effect of topological features on stress-strain behavior of thermosetting systems. The dog-bone shape specimens, as shown in Figure 6.3, were loaded with an INSTRON apparatus under uniaxial extension with a crosshead speed of 1 mm/min at room temperature. Figures 6.6, 6.7, and 6.8 are the representative engineering stress-strain curves for DGEBA – DETDA, DGEBA – PPODA<sub>x=2.5</sub>, and DGEBA – PPODA<sub>x=6.1</sub>, respectively.
Figure 6.6. Representative stress-strain curves for the DGEBA-DETDA systems.
Figure 6.7. Representative stress-strain curves for the DGEBA-PPODA$_{x=2.5}$ systems.
Figure 6.8. Representative stress-strain curves for the DGEBA-PPODA$_{x=6.1}$ systems.
It was shown that the systems that are composed of DGEBA – DETDA have the highest $T_g$ among the thermosetting systems investigated here. The stress-strain curves for these systems did not show large ductility, thus samples broke before yielding. In contrast, systems that were composed of DGEBA – PPODA$_{x=2.5}$, and DGEBA – PPODA$_{x=6.1}$ exhibited larger ductility beyond yielding and before failure. After comparing these three thermosetting systems (Blank curves), one can conclude that the major difference between these systems is $T_g$. In general, $T_g$ is the stress-strain shape determining factor for thermosetting systems. When testing temperature (at which mechanical characterization is conducting) gets closer to the $T_g$ of the testing samples, polymer chains have more freedom for local motion, dissipating the applied stress and delaying the strains at which covalent bonds break. Therefore, the effect of topological variations would be more observable in systems with $T_g$’s closer to the testing temperature. For the thermosetting systems studied in this Chapter, the ones made from DGEBA – PPODA$_{x=6.1}$ had this feature.

Values of Young’s modulus, tensile strength, and failure strain for all the systems are listed in Table 6.2. The average values and the associated standard deviations were measured from at least 8 replicates for each data point.
Table 6.2. Average values of Young’s modulus (E), tensile strength ($\sigma_{\text{max}}$), and elongation at break ($\varepsilon_f$).

<table>
<thead>
<tr>
<th>Thermosetting system</th>
<th>E (GPa)</th>
<th>$\sigma_{\text{max}}$ (MPa)</th>
<th>$\varepsilon_f$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DGEBA-DETDA</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Blank</td>
<td>2.6 ± 0.1</td>
<td>78.5 ± 5.9</td>
<td>5.3 ± 0.9</td>
</tr>
<tr>
<td>cPPODAx=6.1</td>
<td>2.3 ± 0.2</td>
<td>76.2 ± 3.0</td>
<td>5.3 ± 0.7</td>
</tr>
<tr>
<td>cPPODAx=33</td>
<td>2.6 ± 0.2</td>
<td>66.6 ± 9.3</td>
<td>4.9 ± 1.0</td>
</tr>
<tr>
<td>DGEBA-PPODAx=2.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Blank</td>
<td>2.4 ± 0.3</td>
<td>59.0 ± 5.7</td>
<td>5.1 ± 1.9</td>
</tr>
<tr>
<td>cPPODAx=6.1</td>
<td>2.3 ± 0.2</td>
<td>60.0 ± 1.5</td>
<td>6.5 ± 0.7</td>
</tr>
<tr>
<td>cPPODAx=33</td>
<td>2.1 ± 0.2</td>
<td>54.7 ± 0.7</td>
<td>8.6 ± 2.4</td>
</tr>
<tr>
<td>DGEBA-PPODAx=6.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Blank</td>
<td>2.2 ± 0.2</td>
<td>41.0 ± 4.5</td>
<td>29.4 ± 19.6</td>
</tr>
<tr>
<td>cPPODAx=6.1</td>
<td>2.0 ± 0.1</td>
<td>40.4 ± 4.7</td>
<td>52.1 ± 17.4</td>
</tr>
<tr>
<td>cPPODAx=33</td>
<td>1.5 ± 0.1</td>
<td>34.2 ± 1.0</td>
<td>64.6 ± 20.0</td>
</tr>
</tbody>
</table>
As expected, the presence of capped PPODAs reduced Young’s modulus and tensile strength. Larger adducts, capped PPODA$_{x=33}$, dropped these quantities more than the smaller ones, PPODA$_{x=6.1}$. On average, Young’s modulus and strength were not significantly degraded for the polymer networks doped with 5% capped PPODA$_{x=6.1}$.

It is interesting to note the relatively large plastic deformation for the samples with capped PPODA inclusions. This observation was consistent with our observation of ductile thermosetting systems discussed in Chapter 3. As a result of the presence of the capped PPODA, the observed plastic deformation links to the topological variations in polymer networks because inert capped PPODA species are not covalently bonded to the crosslinked structures.

6.3.3. Small Angle X-ray Scattering

To understand the origins of the observed mechanical elongation in the DGEBA – PPODA$_{x=6.1}$ systems, gauge section of the tensile coupons were irradiated with X-ray before and after mechanical extension. A SAXS/WAXS apparatus (Rigaku S-MAX 3000) was utilized for this purpose. Each sample was irradiated with an X-ray beam with a wavelength of 1.54 Å (Cu$_{K\alpha}$) for a duration of 15 minutes. Figures
6.9 and 6.10 show scattered intensity (integrated over the azimuthal angle, $\chi$) versus reciprocal space $q$-vector before and after deformation, respectively.
Figure 6.9. Average scattered intensity of the DGEBA-PPODA$_{x=6.1}$ systems prior to mechanical extension, with average integration over the azimuthal angle ($\chi$).
Figure 6.10. Average scattered intensity of the DGEBA-PPODA$_{x=6.1}$ systems after mechanical extension, with average integration over the azimuthal angle ($\chi$).
The results prior to mechanical deformation revealed no differences between the blank sample and the modified ones (doped with 5% capped PPODA) suggesting that in unstressed situations, the non-bonded heterogeneities do not tend to scatter X-ray beams. However, the graph for the same samples after mechanical extension, revealed significant differences between the blank sample and the samples with 5% inclusion of capped PPODAs. It is evident that a peak in the q-range of 0.015 – 0.05 Å\(^{-1}\) starts to appear for the systems with capped PPODAs inclusions. This could be due to the change in size of the heterogeneous domains, and supports the fact that void opening mechanism causes the observed ductility in glassy state. Upon plastic deformation, molecular surfaces that are formed due to the presence of inert capped PPODAs begin to distort, change in size, and create pore structures around the capped PPODAs. The overall packing (density) reduces in this case. The distorted heterogeneous phase, capped PPODAs, are distinguishable by X-ray beams. The difference between blank samples and modified samples (with 5% capped PPODAs) in the Porod limit, q-value of about 0.16 Å\(^{-1}\), was also detected by X-ray. The difference in shape-factor parameter (S) implies that shape of the heterogeneous domains alter upon mechanical extension.
6.4. Conclusion

Three thermosetting systems with $T_g$’s ranging from 60 °C – 180 °C were investigated. For each individual resin, three blends were prepared, blank, with 5% capped PPODA$_{x=6.1}$ inclusion, and with 5% capped PPODA$_{x=33}$ inclusion. Dynamic mechanical analysis revealed that, per each thermoset, the ones containing 5% capped PPODA$_{x=33}$ show the lowest crosslinking density and $T_g$. Quasi-static tensile properties implied that $T_g$ is the stress-strain shape determining factor. For the thermosetting systems with $T_g$’s close to testing temperature, the effect of induced molecular surfaces (due to presence of the inert capped PPODA) significantly enhanced plastic deformation beyond yielding and prior to rupture. This effect was substantially minimized for the high-$T_g$ thermosets. Because the crosslinkers are stiff in this case, plastic deformation is not likely to occur because molecular motion, localized shear yielding, and void opening mechanisms are considerably restricted though the molecular surfaces are present. SAXS study indicated the deformation (in both size and shape) of the heterogeneous domains upon mechanical extension.
Chapter 7. Synthesis and Characterization of Polymer Network Isomers using Monoamine-functionalized Partially Reacted Substructures (mPRS)

7.1. Introduction

The effect of network structure on mechanical performance of thermosetting polymers was investigated. It was shown that the presence of distinct molecular surfaces (also known as protovoids) improves a material’s ductility without affecting Young’s modulus, strength or glass transition temperature (Chapters 3 and 6). In addition, it was shown that rearranging the molecular structures such that flexible agents create loosely crosslinked domains, rather than randomly dispersed, significantly improved the fracture toughness (Chapter 5). Regardless of the unique thermal and mechanical properties of the polymer network isomers, discussed in Chapter 5, stress-strain curves of these systems did not show plastic deformation in glassy state that was observed in the RES-modified systems (Chapter 3).

It was determined that the lack of plastic deformation for thermosetting systems in glassy state could be due to either relatively high $T_g$, or the absence of molecular surfaces that allow molecular motions without bond breaking.
The effect of $T_g$ was discussed in the previous Chapter. It was shown that $T_g$ is the major shape-determining parameter for the stress-strain curves of thermosetting polymers in glassy state. Accordingly, the substantial plastic deformation in modified polymer networks can never be observed if the crosslinkers are stiff, or polymer $T_g$ is high, even though molecular surfaces are present in the systems. The reason was shown to be due to restriction in molecular motions, localized shear yielding, and void opening.

The material discussed in Chapter 6 provides the preliminary investigation for the studies in this Chapter. Although the results were promising, comparing the mechanical properties of the systems with capped PPODAs was not satisfactory because compositions, and subsequently $T_g$’s, were not the same due to presence of the inert capped PPODAs. In this Chapter, the effect of the molecular surfaces in high $T_g$ thermosts will be investigated. Polymer network isomers with similar compositions and varied molecular structures were synthesized and characterized. The concepts and procedures in this Chapter are very similar to the studies in Chapter 5, excepting that different PRS were used.

Figure 7.1 illustrates the difference between the molecular structures of the systems discussed here and the ones discussed in Chapter 5. The difference between the
systems is the embedded PRS. One was prepared by using diamine curing agents, while the other was prepared by incorporating monoamine curing agents.
Figure 7.1. dPRS-modified vs. mPRS-modified systems; differences in molecular structures.
Experimental design in this Chapter was aimed to replace the loosely crosslinked domains in dPRS-modified systems with nanostructures that could mimic the role of the molecular surfaces (protovoids), as in Chapter 3. In fact, we explored the possibility of synthesizing thermosetting systems with all the advantageous properties, yet exhibit large deformations.

7.2. Experimental

7.2.1. Material

Tetraglycidyl of diaminodiphenylmethane (TGDDM) provided by Sigma-Aldrich and Diglycidel ether of bisphenol-A (DGEBA, EPON 825 - Miller-Stephensen), n=0.07, were used as the epoxy resins. Additionally, polyetheramines, (PEA\textsubscript{600}, Jeffamine M-600, and PEA\textsubscript{1000}, Jeffamine M-1000 – Huntsman) were used as the mono-amine curing agents to formulate the mPRS. PEA\textsubscript{600} are predominately polypropylene glycol (PPG) based with a propylene oxide (PO) to ethylene oxide (EO) ratio of about 9 to 1, whereas PEA\textsubscript{1000} are predominately polyethylene glycol (PEG) based with PO:EO ratio of about 3/19. Moreover poly(propylene-
oxide)diamine (PPODA_{x=2.5}, Jeffamine D230 – Huntsman) was used as the primary curing agent. The molecular structures of these materials are shown in Figure 7.2.
Figure 7.2. Chemical structure of the resins used in this study. (a) tetraglycidyl of diaminodiphenylmethane (TGDDM), (b) Jeffamine Monoamines (M-series) [Upper]: m-600, MW = 600, PO/EO = 9/1, [Lower]: m-1000, MW = 1000, PO/EO = 3/19, (c) Jeffamine Diamines (D-series) D-230, MW = 230, PO ~ 2.5.
It should be noted that the purpose of using TGDDM instead of DGEBA was to form crosslinked structures. If DGEBA resins were cured with PEAs, the fully cured structure would have been a branched polymer, in theory, because the functionality of both resins are two.

7.2.2. Synthesis Procedure

Similar to the procedure cited in Chapter 5, formulation of the polymer isomers involved three steps: (1) Synthesizing the monoamine functionalized Partially Reacted Substructures (mPRS) with controlled extent of polymerizations; (2) making blends of blank samples (TGDDM + PPODA_{x=2.5}) and adding specific contents of the reactive mPRS; and (3) curing the blends.

To study the effect of free-end-branch chain lengths, two different mPRS were prepared and investigated in this study: (1) mPRS-PEA\textsubscript{600} and (2) mPRS-PEA\textsubscript{1000}. They were produced by preparing stoichiometric blends of PEA\textsubscript{600} and PEA\textsubscript{1000} with TGDDM followed by curing at 80 °C. The chemical conversion of these mixtures was monitored using a Nexus 870 FTIR spectrometer (Thermo Nicolet Corp.) in the near IR region. Figure 7.3 shows the fractional conversion of epoxy with respect to time obtained using the peak at 4530 cm\textsuperscript{-1} which corresponds to the stretching and bending of oxirane bands.
Figure 7.3. Chemical consumption of epoxide groups as a measure of the extent of curing reactions for TGDDM together with PEA_{600} and PEA_{1000}. The reaction temperature was at 80 °C.
Curing reactions were stopped at 60% and 80% chemical conversion by removing the samples from reaction condition and cooling to room temperature. The resulting mPRS samples were labelled 60% and 80% conversion mPRS, respectively. Specific amounts of each of the resulting mPRS were then added to stoichiometric blends of TGDDM and PPODA_{x=2.5} to make solutions of 10% and 20% by weight of mPRS. The cured samples were called mPRS-modified samples and were labelled according to their mPRS chemical conversion. Additionally, batches with 10% and 20% by weight of mPRS were prepared without the partial curing step (i.e. 0% conversion). The resulting cured samples were called mPRS-control samples (labelled “0% conversion mPRS”). Samples with the same mPRS content for any mPRS chemical conversion were termed polymer network isomers because they possessed the same overall chemical composition but differ in molecular arrangement of network building blocks. For additional comparison, PEA-free samples (blank samples) were also prepared by curing stoichiometric blends of TGDDM and PPODA_{x=2.5}. All blends were well mixed and degassed with a centrifugal mixer. They were then oven-cured at 80 °C for 24 hours and post-cured at 160 °C for 4 hours.

The importance of consistency should be noted during the curing procedure. If the resin blends for polymer isomers were cured at different curing protocols, i.e. different curing and post-curing temperatures, then topological structure of the
resulting polymers could have differed as a result of changing the substitution factor, \( k_2/k_1 \), as discussed in Chapter 5. Accordingly, \( k_1 \) and \( k_2 \) are temperature dependent, Arrhenius effect. If curing temperature of the control systems was different than curing temperature of the corresponding modified isomers, the differences in network topology could not claim to be solely due to the induced mPRS nanostructures.

7.3. Results and Discussion

7.3.1. Glass Transition Temperature

Similar to the dPRS-modified system isomers, \( T_g \) values for the mPRS-modified system isomers were measured using the TA-Q800 dynamic mechanical analyzer in single cantilever mode. DMA specimens were heated at a temperature ramp rate of 2 °C/min under a cyclic displacement with a frequency of 1 Hz and amplitude of 15 µm. Reported \( T_g \) values were based on the peak position of tan δ curves. Similar to the dPRS systems, \( T_g \) values of the polymer isomers were not the same here. Systems with the highest degree of PRS conversion had the highest \( T_g \). Figures 7.4 and 7.5 show the tan δ curves of the blank, control, and modified samples at 10%
and 20% mPRS-PEA$_{1000}$ content. The reason for the elevated $T_g$ of the modified polymer networks was discussed comprehensively in Chapter 5, and is not discussed herein.
Figure 7.4. Tan δ of the blank, control and mPRS1000-modified systems at 20% mPRS content.
Figure 7.5. Tan δ of the blank, control and mPRS_{1000}-modified systems at 10% mPRS content.
Moreover, tan δ curves for the corresponding polymer isomers reinforced with 10% and 20% mPRS<sub>600</sub> are shown in Figure 7.6 and 7.7. Similar to the observations on dPRS systems (dPRS<sub>4000</sub> vs dPRS<sub>2000</sub>), T<sub>g</sub> difference between the control and the modified systems was mitigated when smaller PEAs molecules (PEA<sub>600</sub>) were used.
Figure 7.6. Tan δ of the blank, control and mPRS\textsubscript{600}-modified systems at 20% mPRS content.
Figure 7.7. Tan δ of the blank, control and mPRS_{600}-modified systems at 10% mPRS content.
The glass transition temperature of the thermosetting systems studied here are listed in Tables 7.1 and 7.2. The reported $T_g$ values are based on the position of peak of tan $\delta$ curves.
### Table 7.1. Glass transition temperature of the thermosets reinforced with PEA_{1000}.

<table>
<thead>
<tr>
<th>mPRS Content</th>
<th>PRS Conversion</th>
<th>$T_g$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0%</td>
<td>163</td>
</tr>
<tr>
<td></td>
<td>60%</td>
<td>141</td>
</tr>
<tr>
<td></td>
<td>80%</td>
<td>148</td>
</tr>
<tr>
<td>0%</td>
<td>144</td>
<td></td>
</tr>
<tr>
<td>10%</td>
<td>134</td>
<td>N/A</td>
</tr>
<tr>
<td>15%</td>
<td>131</td>
<td>149</td>
</tr>
<tr>
<td>20%</td>
<td>125</td>
<td>130</td>
</tr>
<tr>
<td></td>
<td>135</td>
<td></td>
</tr>
</tbody>
</table>

### Table 7.2. Glass transition temperature of the thermosets reinforced with PEA_{600}.

<table>
<thead>
<tr>
<th>mPRS Content</th>
<th>PRS Conversion</th>
<th>$T_g$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0%</td>
<td>163</td>
</tr>
<tr>
<td></td>
<td>60%</td>
<td>141</td>
</tr>
<tr>
<td></td>
<td>80%</td>
<td>148</td>
</tr>
<tr>
<td>0%</td>
<td>144</td>
<td></td>
</tr>
<tr>
<td>10%</td>
<td>134</td>
<td>N/A</td>
</tr>
<tr>
<td>15%</td>
<td>131</td>
<td>149</td>
</tr>
<tr>
<td>20%</td>
<td>125</td>
<td>130</td>
</tr>
<tr>
<td></td>
<td>135</td>
<td></td>
</tr>
</tbody>
</table>
7.3.2. Fracture Toughness

Once samples were fully cured, they were cut into compact tension specimen geometries. A compact tension test was performed under quasi-static tensile loading with the crosshead speed of 1 mm/min following the ASTM D5045.

Values of critical strain energy release rate, $G_{1c}$, were measured using linear elastic fracture mechanics (LEFM). These values are shown in Figures 7.8 and 7.9 for mPRS$_{1000}$ and mPRS$_{600}$, respectively. Average values and the corresponding deviation for each data point were measured from at least 8 replicates.
Figure 7.8. Strain energy release rate, $G_{1c}$, for the mPRS$_{1000}$ systems.
Figure 7.9. Strain energy release rate, $G_{1c}$, for the mPRS$_{600}$ systems.
The results seem to be consistent with the observations from the dPRS systems discussed in Chapter 5. The thermosetting systems reinforced with mPRS-PEA<sub>600</sub> were analogous to the systems reinforced with dPRS-PEA<sub>2000</sub>, such that fracture toughness was not substantially enhanced. Accordingly, when chain length of the curing agents used in the PRS is not large, the synergistic effect of the modified topology on toughness is substantially reduced. In this case, low-T<sub>g</sub> curing agents (PEA<sub>600</sub>) act as tougheners. In other words, mechanical properties of the modified systems, particularly toughness, is not significantly higher than the controls, although topology is varied. One probable explanation for this observation is that when length of the flexible curing agents (PEAs) are small, the control and modified structures are not topologically distinctive, particularly when PRS chemical conversion is not too high. In this case, the synergistic effect of the PRS is minimized, and the fracture behavior of the modified systems is not considerably different than the control systems.

However, when the chain length of the PEAs is large, as in mPRS-PEA<sub>4000</sub> and dPRS-PEA<sub>4000</sub>, the topological differences between control and modified structures become more distinctive. In this case, the effect of modified network topology on mechanical properties is more discerned. This is the case when substantial energy dissipation takes place at the PRS domains via cavitation and plastic void-growth, and delays the catastrophic failure. Figure 7.10 demonstrates the difference in
structural topology between mPRS-modified thermosets and the corresponding controls.
Figure 7.10. Probable structural formation of the polymer network isomers. Control systems (dispersion of PEAs). mPRS-modified systems (Coalesced PEAs).
Figure 7.11 shows the representative SEM micrographs from the fracture surfaces of the blank, control, and mPRS-modified samples, respectively. The control and modified samples were at 10% mPRS content. Fracture surface morphologies of the blank and control samples only varied in roughness. However, fracture surface morphology of the polymer isomers, control vs. mPRS-modified, indicated the presence of cavities. As a result, void opening is the governing mechanism resulting in higher toughness for the mPRS-modified systems.
Figure 7.11. SEM micrographs from the fracture surfaces of Blank, Control, and Modified structures. The control and modified samples were at 10% mPRS content, and the mPRS conversion was at 80%. Scale bars are 1µm in size.
A question arises as to why the increase of PRS chemical conversion is not affecting the $G_{IC}$ values for the batches with 20% mPRS loading. In fact, the same behavior was observed when dPRS was used. In the case of dPRS systems, insensitivity of toughness to PRS conversion was observed above 20% dPRS inclusions. These results are shown in Appendix E. One possible explanation for this observation could be due to the nature of the cracks. As PRS content goes up, final $T_g$ decreases. Considering that testing temperature is constant (room temperature), the samples with relatively high-$T_g$ (when temperature difference between $T_g$ and testing temperature is large) reveals “brittle stable” cracks. As the $T_g$ of the testing samples gets closer to the testing temperature, “brittle unstable” and “ductile” cracks are observed, respectively.\textsuperscript{1, 2} The 20% mPRS samples, similar to the 30% dPRS samples, exhibited brittle unstable (stick/slip) cracks. In these cases, initial failure/slip happened at smaller loadings than the identical systems at lower mPRS contents, hence lower fracture toughness values observed. This observation is justifiable when one recognizes that the tensile strength of the systems with lower mPRS content is lower than that of the systems with higher mPRS content. Lower tensile strength is equivalent to lower load-bearing maximum in a polymer, and subsequently lower fracture toughness. Therefore, unlike PRS conversion, PRS content is not favorable for improving mechanical performance and fracture behavior.
7.3.3. Quasi-Static Tensile Properties

Thus far, it has been shown that the incorporation of mPRS with elevated mPRS chemical conversion improves fracture toughness. However, the fundamental question as to what extent the existing molecular surfaces in the mPRS-modified systems can improve material’s elongation when material’s $T_g$ is relatively high, has yet to be answered.

Dog-bone shape coupons from blank, control and modified resins were casted and cured following the same procedure as described in the “synthesis procedure” of this Chapter. At least 6 specimens from each batch were loaded under a uniaxial extension with a crosshead speed of 1 mm/min using a hydraulic INSTRON apparatus.

Figure 7.12, shows the representative stress-strain curves of the polymer network isomers reinforced with mPRS$_{1000}$ at 20% mPRS loading. Interestingly, the embedded molecular surfaces enhanced the failure strains by more than 100%. Considering the absorbed energy (area under the stress-strain curve), the difference between control and modified systems was even greater. To our knowledge, this stress-strain behavior for high-$T_g$ thermosetting systems below $T_g$ (in glassy state) has never been observed elsewhere. This remarkable elongation in mPRS-modified systems originates from localized polymer chain motions and void opening at the
molecular surfaces. The induced molecular surfaces in polymer network structures allow limited molecular motions without bond breaking. Overall, the mPRS-modified system revealed higher elongation, higher $T_g$, and higher fracture toughness than the corresponding control systems, where tensile strength and modulus were almost equivalent.
Figure 7.12. Representative stress-strain curves for the control, and mPRS-modified systems at 20% mPRS loading.
Figure 7.13 and 7.14 show the representative stress-strain curves of the control and modified systems at different mPRS content. As expected, increasing the mPRS content clearly reduces Young’s modulus and strength; however, the enhanced elongation that was captured in the modified systems was never observed in the controls.
Figure 7.13. Representative stress-strain curves for the control system isomers with compositions corresponding to 0%, 10%, 15%, and 20% mPRS content.
Figure 7.14. Representative stress-strain curves for the modified systems at 0%, 10%, 15%, and 20% mPRS content.
Table 7.3, and 7.4 list the average values of Young’s modulus, tensile strength, and failure strain of the polymer networks reinforced with mPRS$_{1000}$ and mPRS$_{600}$, respectively. The enhanced elongation was not observed for the systems reinforced with mPRS$_{600}$ or the ones with 10% content of mPRS$_{1000}$. The insignificant difference in stress-strain behavior of control and mPRS$_{600}$-modified samples was attributed to the relatively indistinguishable network topologies. When shorter PEAs are used, the effect of network topology on mechanical behavior of thermosetting systems is minimized because differences in network topology are rather small and relatively indistinguishable. However, the lack of large deformation for the samples at 10% mPRS content was not expected. Although a slight increase in failure strain was observed for modified samples in this case, results suggest that mPRS content seems to be a critical factor in determining the level of elongation.
Table 7.3. Average values of Young’s modulus, Tensile strength, and failure strain for the systems reinforced with PEA_{1000}.

<table>
<thead>
<tr>
<th>mPRS Content</th>
<th>Young's Modulus, E (GPa)</th>
<th>Tensile Strength, $\sigma_y$ (MPa)</th>
<th>Failure Strain, $\varepsilon_r$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PRS Conversion</td>
<td>PRS Conversion</td>
<td>PRS Conversion</td>
</tr>
<tr>
<td>0%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0%</td>
<td>2.7 ± 0.1</td>
<td>73.7 ± 6.6</td>
<td>4.5 ± 0.3</td>
</tr>
<tr>
<td>10%</td>
<td>2.8 ± 0.1</td>
<td>61.7 ± 6.6</td>
<td>66.2 ± 2.5</td>
</tr>
<tr>
<td></td>
<td>2.5 ± 0.1</td>
<td>63.5 ± 2.4</td>
<td>3.3 ± 0.9</td>
</tr>
<tr>
<td></td>
<td>2.6 ± 0.2</td>
<td></td>
<td>5.3 ± 0.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>4.6 ± 0.3</td>
</tr>
<tr>
<td>15%</td>
<td>2.4 ± 0.1</td>
<td>61.1 ± 3.4</td>
<td>58.9 ± 2.3</td>
</tr>
<tr>
<td></td>
<td>N/A</td>
<td></td>
<td>3.4 ± 1.3</td>
</tr>
<tr>
<td></td>
<td>2.1 ± 0.1</td>
<td></td>
<td>N/A</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>7.3 ± 2.2</td>
</tr>
<tr>
<td>20%</td>
<td>2.0 ± 0.2</td>
<td>47.9 ± 0.6</td>
<td>45.1 ± 0.6</td>
</tr>
<tr>
<td></td>
<td>1.8 ± 0.1</td>
<td>48.4 ± 0.8</td>
<td>5.4 ± 1.9</td>
</tr>
<tr>
<td></td>
<td>1.6 ± 0.1</td>
<td></td>
<td>9.7 ± 1.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>8.9 ± 2.7</td>
</tr>
</tbody>
</table>
Table 7.4. Average values of Young’s modulus, Tensile strength, and failure strain for the systems reinforced with PEA_{600}.

<table>
<thead>
<tr>
<th>mPRS Content</th>
<th>Young’s Modulus, E (GPa)</th>
<th>Tensile Strength, $\sigma_y$ (MPa)</th>
<th>Failure Strain, $\varepsilon_r$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PRS Conversion</td>
<td>PRS Conversion</td>
<td>PRS Conversion</td>
</tr>
<tr>
<td>0%</td>
<td>2.7 ± 0.1</td>
<td>73.7 ± 6.6</td>
<td>4.5 ± 0.3</td>
</tr>
<tr>
<td>10%</td>
<td>2.7 ± 0.1</td>
<td>2.6 ± 0.3</td>
<td>2.7 ± 0.1</td>
</tr>
<tr>
<td></td>
<td>58.3 ± 5.9</td>
<td>61.5 ± 5.9</td>
<td>69.0 ± 3.6</td>
</tr>
<tr>
<td></td>
<td>3.3 ± 1.8</td>
<td>3.7 ± 1.1</td>
<td>5.1 ± 0.5</td>
</tr>
<tr>
<td>20%</td>
<td>2.2 ± 0.2</td>
<td>2.5 ± 0.1</td>
<td>1.9 ± 0.1</td>
</tr>
<tr>
<td></td>
<td>53.0 ± 3.5</td>
<td>56.6 ± 2.5</td>
<td>52.4 ± 2.1</td>
</tr>
<tr>
<td></td>
<td>3.4 ± 0.4</td>
<td>4.2 ± 0.5</td>
<td>4.7 ± 0.8</td>
</tr>
</tbody>
</table>
7.3.4. Applicability of the PRS Toughening Technique to Other Epoxy Resins

The method of incorporating partially reacted substructures was shown to significantly influence the behavioral characteristics, particularly a material’s ductility. However, it was important to study the applicability of this formulation technique to other thermosetting systems.

One of the widely used epoxy resins is DGEBA. In this section, properties of the thermosetting systems made from DGEBA (EPON 825) and poly(propylene-oxide)diamine (PPODA\textsubscript{x=2.5}, Jeffamine D230 – Huntsman), together with 15% mPRS\textsubscript{1000} at 0% and 80% chemical conversion, were investigated. Additionally, tensile behavior of the DGEBA-based systems was compared to the analogous systems made from TGDDM and Jeffamine D230, where mPRS contents and conversions were the same for both systems.

Figures 7.15 and 7.16 demonstrate the representative stress-strain curves for the control and modified thermosets of DGEBA-based and TGDDM-based epoxy systems, respectively. Additionally, Table 7.5 represents a comparison of the average values of Young’s modulus, tensile strength and failure strains between these two systems. The average values and corresponding errors were measured from at least 3 – 4 replicates for each data point.
Figure 7.15. Representative stress-strain curves for the modified DGEBA systems at 15% mPRS content and the corresponding control systems.
Figure 7.16. Representative stress-strain curves for the modified TGDDM systems at 15% mPRS content and the corresponding control systems.
Table 7.5. Average values of Young’s modulus, Tensile strength, and failure strain.

<table>
<thead>
<tr>
<th>15% mPRS Content</th>
<th>Young’s Modulus, $E$ (GPa)</th>
<th>Tensile Strength, $\sigma_y$ (MPa)</th>
<th>Failure Strain, $\varepsilon_r$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PRS Conversion</td>
<td>PRS Conversion</td>
<td>PRS Conversion</td>
</tr>
<tr>
<td></td>
<td>0%</td>
<td>80%</td>
<td>0%</td>
</tr>
<tr>
<td>DGEBA</td>
<td>2.4 ± 0.1</td>
<td>2.0 ± 0.1</td>
<td>49.8 ± 4.3</td>
</tr>
<tr>
<td>TGDDM</td>
<td>2.4 ± 0.1</td>
<td>2.1 ± 0.1</td>
<td>61.1 ± 3.4</td>
</tr>
</tbody>
</table>
The results clearly indicate the applicability of the mPRS toughening technique to the DGEBA systems. A substantially large deformation was observed for the modified DGEBA systems (more than two times larger than the controls), while modulus and tensile strength were almost identical. This observation was consistent with our earlier observation of TGDDM systems.

However, an indication of strain softening (necking) was noticed in the DGEBA modified systems while no indication was seen in the TGDDM modified systems. The necking could be related to the \( T_g \) of the systems, as discussed in Chapter 6. The DGEBA systems revealed \( T_g \) values of about 81 °C and 84 °C for the control and modified samples, respectively, whereas the values were 134 °C and 149 °C for the samples made from TGDDM. The difference in stress-strain behavior could also be due to the difference in the chemical structure and functionality of the epoxy resins. TGDDM is a tetra-functional resin, as opposed to the di-functional DGEBA. It is also smaller in molecular size than DGEBA. Consequently, fully cured TGDDM systems have a significantly higher crosslinking density and lower molecular weight between crosslinks than DGEBA systems. This might be the reason why the deformation in the modified DGEBA systems is permanent (plastic deformation), while the deformation in the modified TGDDM systems recovered (elastic deformation). In fact, the mPRS-modified systems exhibited nonlinear elastic behavior and behaved like a super elastomer. More in-depth investigation
(molecular simulations) is necessary to elucidate the relationship between the chemical structure of the epoxy resins and the stress-strain behavior for this particular thermosetting system to determine why mechanical behavior of the mPRS-modified DGEBA systems is different than that of the TGDDM systems”.

7.3.5. Advantages of mPRS Resins

The key factor in synthesis and formulation of the PRS (dPRS or mPRS) was to consider the ease of processing. To be largely applicable in industrial settings, the PRS resins must have low viscosity, and low reactivity after reaching a certain chemical conversion. It must show good miscibility with the commercially available resins and curing agents. So far, we have shown that the dPRS_{4000} and mPRS_{1000} are the preferred PRS resins. Although both are known to effectively improve thermal and mechanical properties, mPRS_{1000} is preferable. Experimental rheology on both samples revealed that the room-temperature viscosity of mPRS_{1000} is lower than that of the dPRS_{4000} at the same level of chemical conversion. This is very advantageous from a manufacturing perspective as it significantly ease the material’s processing.

On the other hand, a major concern regarding this technology is the PRS shelf life, while mPRS_{1000} is preferred due to its longer shelf life. Both PEA_{1000} and mPRS_{1000}
crystallize at room temperature. The crystallization and melting point of mPRS\textsubscript{1000} are shown in the DSC thermograph in Appendix F. Therefore, curing reactions are extremely suppressed in solid phase. As a result, reactive PRS remain at the specified chemical conversion, even after very long period of time.

7.3.6. Gelation Delay in the PRS

Another observation during curing reactions of DGEBA/TGDDM and PEAs was the delay (from the theoretical value) in gelation point. Our earlier studies of the dPRS systems indicated delay in gelation points as well. According to Flory-Stockmayer,\textsuperscript{3,4} for a bimodal mixture, the critical extent of reaction at gel point can be measured from the below equation, assuming the reactants are mixed at stoichiometric amounts, and the functional groups have equal reactivity,

\[
X_{gel} = \frac{1}{\sqrt{(f-1)(g-1)}}
\]  

(7.1)

where \(f\) and \(g\) are the functionality of the reactive groups. To get crosslinked structures for the PRS, functionality of at least one of the monomers should be greater than two. Accordingly, for the thermosetting systems studied in Chapter 5 and 7, one monomer has a functionality of two, and the other has four. Therefore,
the theoretical gel point for these systems is approximately 0.5773. However, the observed gelation points for these systems were higher than the theoretical value.

In this study, the approximate gel point was measured using a steady shear viscosity measurement during curing reactions. Gelation is known to happen at the point where steady shear viscosity suddenly jumps to infinity.\textsuperscript{5, 6} The plots of simultaneous chemical conversion and viscosity (combined FTIR-Rheometer) versus reaction time are shown in Appendix H. The experimental gelation points for the DGEBA-PPODA\textsubscript{x=33} and DGEBA-PPODA\textsubscript{x=68} systems were 0.65 and 0.835, respectively.

We have conducted the same measurement for the mPRS systems composed of TGDDM and PEAs. The PEAs used had a rough molecular sizes of 600 g/mol, 1000 g/mol, and 2000 g/mol, respectively. They are labelled as PEA\textsubscript{600}, PEA\textsubscript{1000}, and PEA\textsubscript{2070} herein. The molecular structure of PEA\textsubscript{600} and PEA\textsubscript{1000} was described earlier in this Chapter. PEA\textsubscript{2070} has the same monoamine structure (with one primary amine at one end) which is predominately polyethylene glycol based with PO:EO ratio of about 10/31.

The results of simultaneous chemical conversion and steady shear viscosity measurement vs. reaction time for each individual system are shown in Figures 7.17, 7.18, 7.19, and 7.20, respectively. It was clearly observed that the gelation
points deviate even more (from the theoretical limit) than in the dPRS systems. The
gelation point for the TGDDM-PEA$_{600}$ and TGDDM-PEA$_{1000}$ were very close to the
full conversion, yet it was never observed for the TGDDM-PEA$_{2070}$ system, even at
higher curing temperature (160 °C), Figure 7.20.
Figure 7.17. Simultaneous extent of cure and viscosity vs. reaction time for the TGDDM-PEA₆₀₀ system at 80 °C. The dashed line represents the approximate gelation point.
Figure 7.18. Simultaneous extent of cure and viscosity vs. reaction time for the TGDDM-PEA$_{1000}$ system at 120 $^\circ$C. The dashed line represents the approximate gelation point.
Figure 7.19. Simultaneous extent of cure and viscosity vs. reaction time for the TGDDM-PEA\textsubscript{2070} system at 120 °C. The dashed line represents the approximate gelation point.
Figure 7.20. Simultaneous extent of cure and viscosity vs. reaction time for the TGDDM-PEA$_{2070}$ system at 160 °C. The dashed line represents the approximate gelation point.
The fact that epoxy, primary amine, and primary-secondary amine peaks disappear at the same time implies that chemical reactions are in the desired pathway, yet on-stoichiometry. NearIR spectra for each of these systems are shown in Figures 7.21, 7.22, 7.23, and 7.24, respectively. In these spectra, the secondary amine peaks are clearly disappeared. This suggests that crosslinkers must form, resulting in formation of network structures. Thus, the observed deviation of gel point from the theoretical limit is not an artifact.
Figure 7.21. NearIR spectra during the TGDDM-PEA₆₀₀ reactions at 80 °C.
Figure 7.22. NearIR spectra during the TGDDM-PEA_{1000} reactions at 120 °C.
Figure 7.23. NearIR spectra during the TGDDM-PEA\textsubscript{2070} reactions at 120 °C.
Figure 7.24. NearIR spectra during the TGDDM-PEA$_{2070}$ reactions at 160 °C.
The probable explanation for the significant deviation of gel point from the theoretical limit is chain cyclization due to lack of substitution. In Chapter 5, we showed that the substitution factor, $k_2/k_1$, decreases with increasing molecular size of the PEAs, explained by the steric hindrance effect. For the bulkier molecules, the reactivity of the secondary amines are substantially suppressed when primary amines are already reacted because the molecular collision is hindered by the massive non-reactive backbone of the molecule. The theoretical limit assumes equal reactivity of primary amines to secondary amines, which means that substitution factor, $k_2/k_1$, equals to 0.5. However, when substitution factor lowers, linear chains must appear first (primary amines react first), followed by the subsequent crosslinking formation (secondary amines reactions) when large fraction of primary amines already reacted. This is the case that happens in DGEBA-dPEA$_{2000}$, DGEBA-dPEA$_{4000}$, TGDDM-PEA$_{600}$, and TGDDM-PEA$_{1000}$ systems. In the limit of dilution, as in TGDDM-PEA$_{2070}$, when the molecular size is substantially large and the molar concentration of reactive groups is small, gelation will never happen, as shown in Figures 7.19 and 7.20. In this case, we believe each TGDDM is capped with two PEA$_{2070}$ without forming a network structure, even though the functionality of TGDDM is 4. The inert structure from the resulting adduct in this reaction is illustrated in Figure 7.25. For this reason, PEA$_{2070}$ was not used in the preparation of mPRS, even though the molecular size was large and, in
theory, could potentially improve the thermal and mechanical behavior of the cured thermosets.
**Figure 7.25.** Probable reaction pathway for the TGDDM-PEA$_{2070}$. 
7.4. Conclusion

A new synthetic strategy was designed and overviewed. The technique was similar to the one presented in Chapter 5, except that monoamine polyetheramines (PEAs) were used instead of diamine PEAs. The technique was termed monoamine functionalized Partially Reacted Substructures, or mPRS. The advantage of using monoamine is that PEAs bond to polymer network structures from one side, leaving a free-end on the other side. This could theoretically create topological features that mimic the role of the molecular surfaces as in the RES-modified systems. As expected, the mPRS-modified thermosets revealed higher fracture toughness and $T_g$ than the corresponding control systems, and without any noticeable influence on modulus and strength. However, the promising observation was the considerably large plastic deformation for some of the mPRS-modified systems. The observed ductility is systematically due to the extension of the molecular surfaces that were captured in the SEM micrographs as voids on the fracture surfaces. The mPRS toughening technique was shown to be successfully extended to other thermosetting systems (DGEBA epoxy resins was examined in this study). To our knowledge, this unique characteristic behavior has never been observed in high-$T_g$ thermosetting systems in glassy state, and thus could result in developing a new generation of epoxy resins for manufacturing high performance structural and composite materials, durable coatings, strong adhesives, etc.
7.5. List of References


4. Flory, P. J. Journal of the American Chemical Society 1941, 63, (11), 3083-3090.


Chapter 8. Conclusions and Recommendations for Future Work

8.1. Conclusions

The interest in epoxy thermosetting polymers is widespread. Boeing 787 Dreamliner, windmill blades, automobiles, coatings, adhesives, etc. are all examples of their different applications, and a demand still exists for improving toughness of these materials while maintaining other advantageous properties such as strength, Young’s modulus, T_g, etc. This study provides a novel approach for improving the intrinsic behavioral characteristic of these polymers that can be potentially extended to all thermosets.

Novel synthetic techniques were developed and adopted, through which polymer networks with the same overall compositions but varying in network topology are synthesized. These systems are referred to as “polymer network isomers”. The synthesis procedure and post-processing characterizations assured that the network structural variations were in the size range of 5-50 nm.

Accordingly, Chapter 3 introduced a novel processing technique termed reactive encapsulation of solvent/drying, or RESD. It was found that without altering
chemical structure, the network topology of a dense thermoset can be engineered such that, under deformation, nanometer-sized cavities (15-25 nm) open and dissipate energy before rupturing covalent bonds, producing a tougher material without sacrificing ultimate tensile strength, modulus, density, or glass transition temperature. SEM images from the fracture surfaces showed clear voids on the modified samples, whereas prior to tension, all modified samples had the same density, $T_g$, Young’s modulus of the unmodified epoxy. Using atomistic simulations, it was shown that during-cure solvent species affect the directionality of the forming covalent bonds. The presence of distinct topological features in the modified network is likely the origin of the large improvement in ductility.

In Chapter 4, we examined the use of equilibrium swelling and glass transition temperature to characterize polymer networks that were cured in the presence of an inert solvent followed by a supercritical drying of the solvent. Three different epoxy resins with different molecular sizes were cured with the same curing agent. We have shown that the traditional swelling model is inadequate to accurately represent the swelling behavior of epoxy-amine gels when prepared in extremely dilute environments. The model was adjusted by incorporating a probabilistic factor based on the probability of finding an elastic chain in the porous structure. The end results implied that the values of molecular weight between crosslinks are insensitive to the amount of solvent present during cure, and in fact, the presence
of inert solvent species changes the direction of the forming covalent bonds and thus alters the network topology by creating molecular surfaces.

The synthetic methodology to develop thermosetting systems with altered topology presented in Chapter 3 was not cost efficient and scalable. Instead, in Chapter 5, a solvent-free based approach is presented. This technique is termed as partially reacted substructures, or PRS. Polymer networks with altered topology were obtained through the addition of a single processing step. A low-$T_g$ thermoset at different extents of polymerization was embedded into a high-$T_g$ majority-phase thermoset. It was shown that the PRS-modified samples are tougher than the corresponding controls, and the toughness is directly proportional to the chemical conversion of the embedded PRS. The major fracture mechanism responsible for the increased energy dissipation was found to be nano-cavitation. SAXS studies revealed that the synthetic method produced controlled heterogeneous structures with nanodomains ranging from 12-25 nm. These nanodomains were determined to be responsible for the onset of cavitation that was quantified using SEM image analysis. Also observed, was that the glass transition temperatures of the modified systems were higher than those of the control systems. In addition, quasi-static mechanical extension did not show substantial differences in mechanical strength and modulus between system isomers.
It was shown that network topology can be used to tailor the behavior of thermosetting materials without the incorporation of toughening agents that often reduce processing ease and are costly. However, the lack of significant elongation of the PRS-modified systems remained paramount. This could be due to either: (1) the large difference between the $T_g$ of the polymer and the testing temperature; or (2) the absence of the molecular surfaces, which could mimic the role of the potential voids in the RES-modified systems.

Chapter 6 discussed the effect of a material’s $T_g$ on its behavioral characteristics. Accordingly, three different epoxy-amine resins with final $T_g$’s ranging from 60 °C – 180 °C were investigated. Per each individual resin, three blends were prepared, blank, with 5% capped PPODA$_{x=6.1}$, and with 5% capped PPODA$_{x=33}$. Dynamic mechanical analysis revealed that, per each thermosetting system, the ones contain 5% capped PPODA$_{x=33}$ showed the lowest crosslinking density and $T_g$. Quasi-static tensile properties revealed that $T_g$ is a major stress-strain shape determining factor. For the thermosetting systems with $T_g$’s close to the testing temperature, the induced molecular surfaces, which was the result of the presence of the inert capped PPODA species, noticeably improved the plastic deformation beyond yielding and prior to rupture. SAXS study indicated the deformation (in both size and shape) of the heterogeneous domains during mechanical extension. However, the observed ductility was substantially minimized for the high-$T_g$ thermosets.
Because the crosslinkers are stiff in this case, the plastic deformation is not likely to occur, and the void opening mechanism is considerably restricted, even though the molecular surfaces are present.

In order to be able to make a clear discussion on the effect of the molecular surfaces on the mechanical properties of high-$T_g$ thermosetting systems, we must compare materials with the same compositions (polymer isomers). The argument in the discussion of Chapter 6 is that we were not comparing the polymer network isomers, and thus the presence of the capped PPODAs could have had deteriorating effects on the mechanical performance.

Therefore, a new synthetic strategy was designed and introduced in Chapter 7. The technique was quite similar to the one presented in Chapter 5, except monoamine polyetheramines (PEAs) were used instead of diamine PEAs. The technique was termed monoamine functionalized partially reacted substructures, or mPRS. The benefit of using monoamine is that PEAs bond to polymer network structures from one side, leaving a free-end on the other side. This could theoretically create topological features that mimic the role of the molecular surfaces as in the RES-modified systems. As expected, the mPRS-modified thermosets revealed higher fracture toughness and $T_g$ than the corresponding control systems without any noticeable influence on modulus and strength. However, the promising
observation was the considerably large plastic deformation for some of the mPRS-modified systems. The observed ductility is systematically due to the extension of the molecular surfaces that were captured in the SEM micrographs as voids on the fracture surfaces. The mPRS toughening technique was shown to be successfully extended to other thermosetting systems (DGEBA epoxy resins was examined in this study). To our knowledge, this unique behavior has never been observed in high-$T_g$ thermosetting systems in glassy state, and it could result in developing a new generation of epoxy resins for manufacturing high performance structural and composite materials, durable coatings, strong adhesives, etc.

It was demonstrated that network topology can be used to tailor physical, thermal and mechanical properties of thermosetting polymers. The experimental methodologies in this dissertation can directly and economically be applied to formulate new epoxy-amine systems for various applications. Although topology-based toughening was investigated on epoxy-amine polymers, the concept can be extended to most thermoset chemistries and perhaps to other brittle network forming materials.
8.2. Recommendation for Future Directions

Although major advances have been achieved in understanding the effect of topology on thermal and mechanical properties of thermosets, there is room for further investigation that could enable one to design materials with tailored properties for particular applications. Some of the possible routes for future advancement in this research include:

- Tuning and scaling-up the introduced synthetic methodologies.

- Investigating the mechanical characteristics of the composite materials when new resin formulations and methodologies are used.

- Studying an in-situ SAXS/SANS to carefully capture the deformation of molecular surfaces during mechanical tension or compression.

- Understanding the structure and probable applications of adducts when very large monoamine PEAs react with an epoxy.

- Investigating the effect of molecular symmetry on the substitution factor. Comparing diamine PEAs to monoamine PEAs.
• Understanding the effect of topological variations on transport properties such as, thermal conductivity and relative mass diffusivity of particular molecules. The impact of this study would consist of synthesizing selective polymer membranes and non-permeable to semi-permeable coatings.

• Embedding pressure/temperature sensitive domains in polymer network structures that could be triggered upon mechanical or temperature shocks, so to change the material properties to withstand the applied stress. One way is to take advantage of thermo-reversible (e.g. Diels-Alder) reactions. Under extreme dynamic environments (such as impacts), temperature rises. If domains have the constituents of DA reactions upon heating, the “molecular surfaces” form via debonding the DA reactants. This could allow the material to absorb more energy without failure. Upon cooling, the bonds will form again, and the material regains its advantageous properties.

• It is suggested to use the difunctional curing agents with two secondary amines (NH) at each end. Jefflink® (Huntsman) and Clearlink 1000® (Dorf Ketal) are examples of the curing agents that can be used herein. These curing agents can be furan-functionalized using furfuryl glycidyl ether and could be used in reversible bonding via DA reactions.
Appendix A. Mathematical Derivation of the Adjusted Dusek Equation

According to Flory,\textsuperscript{1} for a crosslinked polymer gel immersed in a solvent and allowed to reach equilibrium, the two opposing forces that are determining the state of equilibrium are: the thermodynamic force of mixing and the retractive force of polymer chains. State of equilibrium is defined when these two forces counterbalance each other and the total energy of the system is minimized.

$$\Delta F = \Delta F_m + \Delta F_{el}$$  \hspace{1cm} (A.1)

The contribution of mixing can be quantified as

$$\Delta F_m = kT[n_1 \ln(v_1) + \chi_1 n_1 v_2]$$  \hspace{1cm} (A.2)

where $k$ is the Boltzmann constant, $T$ is absolute temperature, $n_1$ is the number of solvent molecules, $v_1$ and $v_2$ are the solvent and polymer volume fraction respectively, and $\chi_1$ is the interaction parameter.

The free energy change due to elastic retractive force is as follow:
\[ \Delta F_{el} = \frac{3\kappa v T}{2} (\alpha_s^2 - 1 - \ln(\alpha_s)) \] (A.3)

Here, \( v \) is the number of elastic chains. In addition, the elongation ratio, \( \alpha_s \), for an isotropically swollen gel can be calculated from volume fraction of PN in swollen state, \( v_{2s} \), via

\[ \alpha_s^3 = \frac{1}{v_{2s}} \] (A.4)

Incorporating the modifying factor, \( P_v \), in the elastic term, we have the contribution to the total free energy change due to elastic retractive force as follows:

\[ \Delta F_{el} = \frac{3\kappa v (P_v) T}{2} (\alpha_s^2 - 1 - \ln(\alpha_s)) = \frac{3\kappa v (v_{2r}) T}{2} (\alpha_s^2 - 1 - \ln(\alpha_s)) \] (A.5)

Therefore, the total free energy change due to swelling can be rewritten as

\[ \Delta F = \kappa T [n_1 \ln(v_1) + \chi_1 n_1 v_1] + \frac{3\kappa v (v_{2r}) T}{2} (\alpha_s^2 - 1 - \ln(\alpha_s)) \] (A.6)

According to equilibrium swelling theory, the equilibrium criterion is

\[ \mu_1 - \mu_1^0 = \frac{\delta \Delta F}{\delta n_1} = 0 \] (A.7)

Substituting, rearranging and solving the above equation, using the definition of \( \alpha_s \) and \( v = \frac{\nu}{v_p M_c} \), the adjusted Dusek model for measuring molecular weight between
crosslinks in highly porous polymer networks or gels formed in extremely dilute environments is as following:\(^2\)

\[
M_c = -\frac{\nu \nu_2^2 \left[\left(\frac{\nu_2}{\nu_2^2}\right)^{\frac{1}{3}} - \frac{1}{2} \left(\frac{\nu_2}{\nu_2^2}\right)\right]}{\nu \nu_1^2 \left[\ln(1 - \nu_2) + \nu_2 + \chi_1 \nu_2^2\right]} \tag{A.8}
\]


Appendix B. DSC Thermographs of the Porous Polymers

A small cut from the supercritically dried gels was tested with DSC. For the samples cured in presence of the inert solvent, an exothermic peak was observed in the first heating scan. The results are displayed in Figure B.1. It is believed that the exotherms appear primarily due to the release of interfacial surface energy upon collapsing the pore walls, as well as relaxation of the polymer chains. The supercritical extraction of solvent removes the solvent species but creates nano-scale pore structures in place. Interestingly, exothermic enthalpy increases with increasing initial solvent content suggesting that thermosets could be tailored by varying the during-cure inert solvent as discussed comprehensively by Raman et al. The second temperature scan didn’t show any exothermic peak implying that all the pore structures have been collapsed in the first heating cycle. Also, the values of glass transition temperature for the supercritically dried samples, were measured at the inflection point of the heat flow vs. temperature curves in the third heating cycle, as shown in Figure B.2.
Figure B.1. DSC first heating scans on the super-critically dried gels (aerogels) for 0, 0.5, 1, 3 TEA specimens (Epon828-PACM).
Figure B.2. DSC third heating scans on the super-critically dried gels (aerogels) for 0, 0.5, 1, 3 TEA samples (Epon828-PACM). The temperature at which inflection point is occurring is where the $T_g$ is reported.
Appendix C. Comparing the Experimental Mc Values to the Theoretical Values

The experimentally measured $M_c$ values for the dense polymer networks, 0 TEA, based on equilibrium swelling technique were compared to the theoretical values. Two separate approaches were used to calculate the $M_c$ values based on the molecular weight of the monomer resins. According to the first model, molecular weight between crosslinks, $M_c$, was determined by the resin molecular size and reaction stoichiometry at some specific curing conversions based on the following formula:\(^1\)

$$
\overline{M_c} = \frac{M_T - M_T \ast 4(1 - X_n)}{\left[3 - 4(1 - X_n)\right]} \quad \left[3 - 12(1 - X_n)\right] \quad (C.1)
$$

$$
M_T = MW_a + \frac{b}{a} MW_e \quad (C.2)
$$

Here, a and b are the initial number of moles of amine and epoxy, respectively; $MW_a$ and $MW_e$ are their corresponding mole weights, and $X_n$ is the epoxy conversion which is assumed to be 1 in our calculations for dense polymer networks.

In the second approach, $M_c$ was calculated from stoichiometry by the following equations:\(^2\)
Here, $M_e$ is the epoxide equivalent weight of the resin, $f$ and $M_f$ are the functionality and molar weight of $f$-th functional amine, and $\Phi_f$ is the mole fraction of amine-hydrogens provided by the $f$-th functional amine.

The measured $M_c$ values and the calculated $\overline{M_c}$ are listed in Table C.1. Comparing the first two columns in Table C.1 indicates that for Epon828-PACM system, the measured $M_c$ value is comparable to the corresponding value determined by eqn. (C.1) and (C.3). This suggests that significantly homogenous polymer networks are being formed through step-growth polymerization for the first case, Epon828-PACM. The measured values tend to deviate from the calculated values for the other two systems where resins with larger molecular size were used. The observed inconsistency between measured $M_c$ values and calculated $\overline{M_c}$ could be due to the non-idealities forming in network structures during step-growth polymerization when resins with larger molecular size were used. In addition, comparing the calculated $\overline{M_c}$ in the third column with the measured $M_c$ values
do not show any consistency, implying that the Crawford model is not adequate for measuring the theoretical $M_c$ values for the systems investigated in this study.
Table C.1. $M_c$ values of the dense polymer networks; 1) Measured by the adjusted Dusek model, 2) Calculated from the molecular size of the resins (using Vakil et al. model), 3) Calculated from the molecular size (using Crawford et al. model).

<table>
<thead>
<tr>
<th>System</th>
<th>$M_c$ (measured)</th>
<th>$\overline{M_c}$ (Vakil et al.)</th>
<th>$\overline{M_c}$ (Crawford et al.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Epon828-PACM (0 TEA)</td>
<td>302</td>
<td>321</td>
<td>481</td>
</tr>
<tr>
<td>Epon836-PACM (0 TEA)</td>
<td>374</td>
<td>487</td>
<td>730</td>
</tr>
<tr>
<td>Epon1001F-PACM (0 TEA)</td>
<td>461</td>
<td>787</td>
<td>1180</td>
</tr>
</tbody>
</table>

Appendix D. MATLAB code for solving the system of ODEs

```matlab
clc
clear T Y k1 k2 sse A B inits E C
global k1 k2 inits
init_E = 0.4318;
init_PA = 0.2159;
init_OH = 0.1;
t_span = 1:51;
inits = [init_E init_PA 0 0 init_OH];
m = 0;
i = 0;
for k1 = 0.1:0.001:0.2
    i = i + 1;
j = 0;
    for k2 = 0.02:0.001:0.06
        j = j + 1;
        [T,Y] = ode45(@PRS,t_span,inits);
m = m + 1;
        B(:,:,m) = Y;
        for k = 1:2
            sst(i,j,k) = sum((Y(:,k) - mean(Y(:,k))).^2);
sse(i,j,k) = sum((Y(:,k) - Expr(:,k)).^2);
            rsquare(i,j,k) = 1 - sse(i,j,k)/sst(i,j,k);
        end
        E(i,j) = (sse(i,j,1)+sse(i,j,2))/2;
end
end
% plot(T,Y(:,1),'-',T,Y(:,2),'-',T,Y(:,3),'-',T,Y(:,4),':')
```
function dy = PRS(t,y)
    global k1 k2 inits
    dy = zeros(5,1);    % a column vector
    dy(1) = -k1*y(1)*y(2)*(inits(5)+y(3)+2*y(4)) - k2*y(1)*y(3)*(inits(5)+y(3)+2*y(4));
    dy(2) = -k1*y(1)*y(2)*(inits(5)+y(3)+2*y(4));
    dy(3) = k1*y(1)*y(2)*(inits(5)+y(3)+2*y(4)) - k2*y(1)*y(3)*(inits(5)+y(3)+2*y(4));
    dy(4) = k2*y(1)*y(3)*(inits(5)+y(3)+2*y(4));
    dy(5) = k1*y(1)*y(2)*(inits(5)+y(3)+2*y(4)) + k2*y(1)*y(3)*(inits(5)+y(3)+2*y(4));
Appendix E. Strain Energy Release Rate

Figure E.1. Values of strain energy release rate at higher loading of dPRS (30% weight) is shown.
Appendix F. Crystallization Point of the mPRS\textsubscript{1000} Systems

Figure F.1. DSC thermographs of the stoichiometric blend of TGDDM and PEA\textsubscript{1000}. Exothermic peaks are upward.
Figure G.1. Representative stress-strain curves for the control, and mPRS_{1000}-modified systems at 10% mPRS loading.
Figure G.2. Representative stress-strain curves for the control, and mPRS$_{600}$-modified systems at 20% mPRS loading.
Figure G.3. Representative stress-strain curves for the control, and mPRS$_{600}$-modified systems at 10% mPRS loading.
Appendix H. Viscosity Measurement versus Cure Kinetics

Figure H.1. Viscosity measurement of the stoichiometric blends of DGEBA and PPODA (x = 2.5, 6.1, 33, 68). The testing temperature was at 80 °C.
Figure H.2. Simultaneous FTIR, Rheology on a stoichiometric mixture of DGEBA-PPODA$_{x=68}$ at 80 °C. The experimental gelation point was around 83.5% conversion.
Figure H.3. Simultaneous FTIR, Rheology on a stoichiometric mixture of DGEBA-PPODA$_{x=33}$ at 80 °C. The experimental gelation point was around 65% conversion.
Vita

Majid Sharifi was born in Mashhad, Iran on January 23, 1987. He graduated from Petroleum University of Technology (former Abadan Institute of Technology) in Abadan, Iran in 2009 with a B.Sc. degree in Petroleum Engineering – Safety and Technical Protections. After receiving his B.Sc. degree in Petroleum Engineering, he worked at Schlumberger, the oil service company, for a couple of months. In 2010, he was admitted into the graduate Chemical Engineering program at Drexel University where he pursued his doctoral research on designing and synthesizing high performance thermosetting polymers under the supervision of Prof. Giuseppe Palmese. Majid’s dissertation on high performance polymers resulted in a number of outstanding research awards recognized by the professional organizations such as Adhesion Society, SAMPE, TAFDV, etc., one book Chapter, several peer-reviewed journal articles and conference proceedings, and at least three additional publications forthcoming. He has given several talks at professional conferences and scientific societies. He is currently a member of the American Chemical Society, American Physics Society, and SAMPE. Majid was selected as outstanding Ph.D. student of the year of 2014 by the Chemical and Biological Engineering department. In 2015, he was recognized and awarded the Drexel outstanding doctoral dissertation in physical and life sciences.