Abstract Molecular Toughening of Epoxy Networks Ian Matthew M<sup>⊆</sup>Aninch Advisor: Giuseppe Palmese, Ph. D. Co-Advisor: John La Scala, Ph. D.

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

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

Bimodal amine distributions were made using polyetheramines of various molecular weights. When cured with a rigid epoxy, the resulting networks, compared to single-distributions networks, had similar bulk cross-link densities but broader glass

transitions and lower modulus due to local network heterogeneity. The fracture behaviors were altered but the toughness did not improve. Polydisperse epoxy distributions, with dispersity indices ranging from 1.8 to 10.7, when cured with a linear amine, had no noticeable impact on the network properties.

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

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