Ionic Liquid-Modified Thermosets and Their Nanocomposites: Dispersion, Exfoliation, Degradation, and Cure

This dissertation explores the application of a room temperature ionic liquid (RTIL) to problems in the chemistry, processing, and modification of thermosetting polymers. In particular, the solution properties and reaction chemistry of 1-ethyl-3-methyl imidazolium dicyanamide (EMIM-DCN) are applied to problems of nanoparticle dispersion and processing, graphite exfoliation, cyanate ester (CE) cure, and the environmental degradation of CEs.

Nanoparticle Dispersion

Nanocomposite processing can be simplified by the use of the same compound as both a nanoparticle solvent and an initiator for polymerization. This dual-function molecule can be designed both for solvent potential and reaction chemistry. EMIM-DCN, previously shown by our lab to act as an epoxy initiator, is used in the synthesis of silica, acid expanded graphite nanoplatelet (GNP) composites as well as hybrid composites containing both silica and GNPs. These composites show excellent dispersion as well property improvements. Notably, Silica composites show a simultaneous increase in modulus and fracture toughness. GNP nanocomposites show a 70% increase in modulus along with a 10-order of magnitude increase in electrical conductivity at 6.5 vol%, and an electrical percolation threshold of 1.7 vol%. Hybrid silica-GNP composites showed a synergistic reinforcement effect, resulting in a 250% modulus improvement relative to the original epoxy.

Direct Graphite Exfoliation By Laminar Shear

This work presents an laminar-shear alternative to chemical processing and chaotic flow-fields for the direct exfoliation of graphite and the single-pot preparaton of nanocomposites. The resulting nanocomposite shows low electrical percolation (0.5 vol%) and low thickness (1-3 layer) graphite/graphene flakes by TEM. The theory of laminar flow of layered crystals through a 3-roll mill is analyzed and applied to the latest developments in the graphite interlayer shear stresses, providing an understanding of the relationship between processing

Cyanate Ester Degradation

Cyanate ester systems offer high-temperature promise, but this potential is vulnerable to hydrolytic degradation which can blister the resin, decrease its cross-linking density, and reduce high-temperature performance. This study examines the hydrolytic degradation of cyanate esters without catalyst, with conventional catalysis, with an RTIL catalyst, and graphite nanocomposites of CE cured with an RTIL catalyst. Diffusion coefficients, equilibrium water sorption, reaction rates, and glass transition temperature changes are determined, showing the effect of cure schedule, processing, and composite on degradation performance.

Cyanate Ester Cure

This project creates a novel, ionic thermoset polymer. Diverse dicyanamide-containing RTILs were found to initiate polymerization of bi- and tri-functional cyanate esters. The dicyanamide initiator provides an alternative to metal and hydroxyl catalysts (which have been shown to accelerate degradation and possess human and environmental toxicity). Additionally, the ionic character of the new polymer, rare among thermosets, lends itself to future research and novel applications. RTIL initiation also paves the way to new CE technologies, including RTIL-CE nanocomposites, prepared by graphite exfoliation and nanocomposite dispersion techniques developed elsewhere in this dissertation.