CASE STUDY

Exploration and Validation of Polycyanurate Thermoset Crosslinking Mechanisms

Molecular dynamics simulations accelerate the development and optimization of next-generation aerospace materials

Executive Summary

- **Accurately predicted key thermophysical properties** such as glass transition temperature (T_g), density, and coefficient of thermal expansion for the polycyanurate systems

- **Built realistic polycyanurate models** for the first time from its constituent di(cyanate ester) monomer rather than using prebuilt triazine moieties

- **Effectively modeled water uptake and location in thermoset matrix** by penetrant loading and radial distribution function analysis

- **Proposed an alternative water uptake mechanism for polycyanurate** that was not observed via experimental methods

- **Enabled rational design** of high performance thermosetting polymers
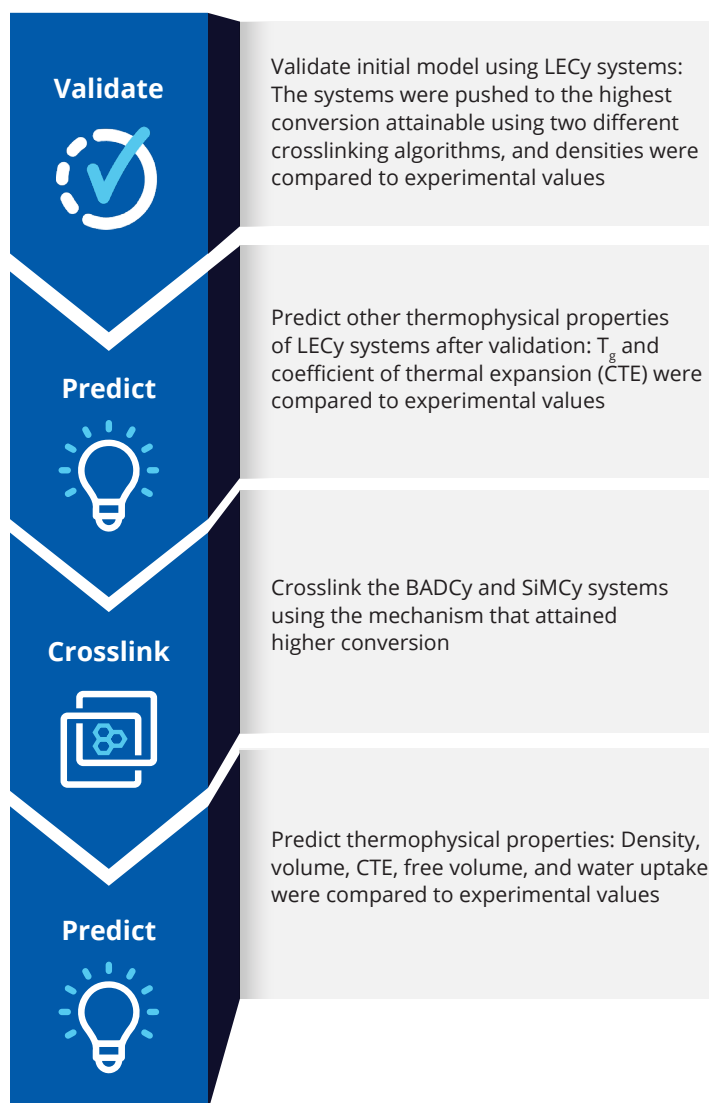

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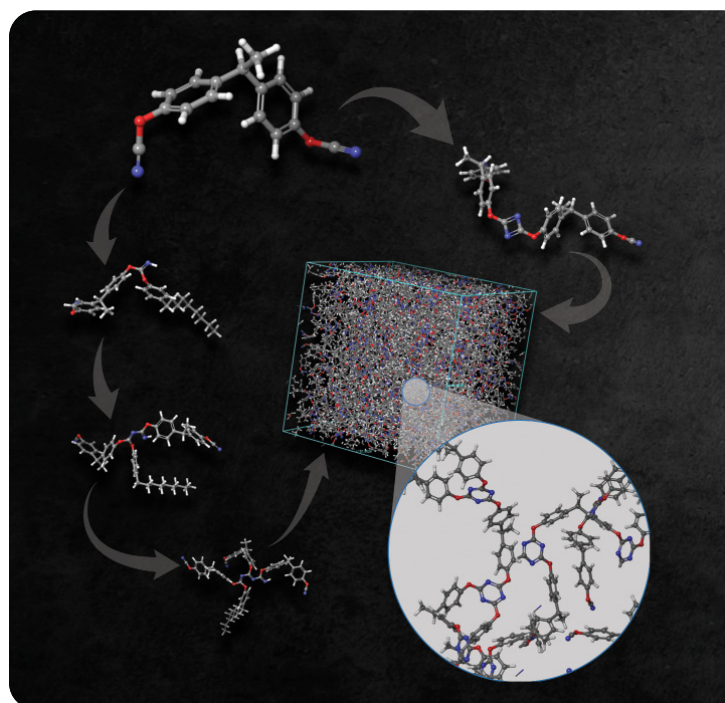
Challenges

Thermosetting polymers such as polycyanurates are important for high temperature applications in aerospace because of their performance properties, such as high glass transition temperatures (T_g) and exceptional flame resistance. Modeling and simulation efforts have enabled rapid screening of candidate materials with targeted properties for high performance applications without dedicating the significant time and resources required for wet chemistry. However, there are challenges for predicting properties of thermosetting polymers like polycyanurates:

- The reactions, such as curing/crosslinking, are often complicated and require multiple factors to consider

- Iterative crosslinking simulation for large cells containing thousands of reactive groups was not possible until recent years with the advances of GPU-accelerated molecular dynamics (MD) simulations

- Generating a realistic model system is paramount in the prediction of properties and study of the dynamics, however, there are exceedingly few examples of in situ crosslinking of di(cyanate esters) for polycyanurate systems

Approach

Scientists from Air Force Research Laboratory (AFRL) and Schrödinger worked together to build realistic polycyanurate models from its constituent di(cyanate ester) monomer rather than using prebuilt triazine moieties, as well as explore the crosslinking mechanisms. All chemical models were built and simulations performed using the Schrödinger Materials Science Suite and Desmond MD system:

Validate

Validate initial model using LECy systems: The systems were pushed to the highest conversion attainable using two different crosslinking algorithms, and densities were compared to experimental values

Predict

Predict other thermophysical properties of LECy systems after validation: T_g and coefficient of thermal expansion (CTE) were compared to experimental values

Crosslink

Crosslink the BADCy and SiMCy systems using the mechanism that attained higher conversion

Predict

Predict thermophysical properties: Density, volume, CTE, free volume, and water uptake were compared to experimental values

LECy: bisphenol E dicyanate ester
BADCy: bisphenol A dicyanate ester
SiMCy: silicon-containing analogue of BADCy

Results

This work uses MD simulations to form polycyanurate networks in order to predict thermophysical properties and probe water uptake and aggregation behavior at the atomistic level. The predictive power of this model is considered adequate for further study of other polycyanurate systems, whether in formulation or synthesis of novel monomers to evaluate properties like water uptake or for mechanical property prediction of systems employing these and other cyanate ester materials.

- Thermophysical properties (T_g, density, CTE) of the LECy systems crosslinked via the two different mechanisms aligned well with experimental data

- Multiple thermophysical properties were probed for BADCy and SIMCy systems, and the simulated data showed rank ordering in line with the experiment

- Water overwhelmingly tended to aggregate together in free volume, rather than closely associated near specific moieties. However, polar moieties like triazine rings and phenolic groups showed an affinity to the water and tended to reside on the periphery of the free volume where the water is located

- New hypothesis was proposed: Increased hydrophobicity is the driving factor in the decreased water uptake of SiMCy rather than a change in free volume in the SiMCy monomer
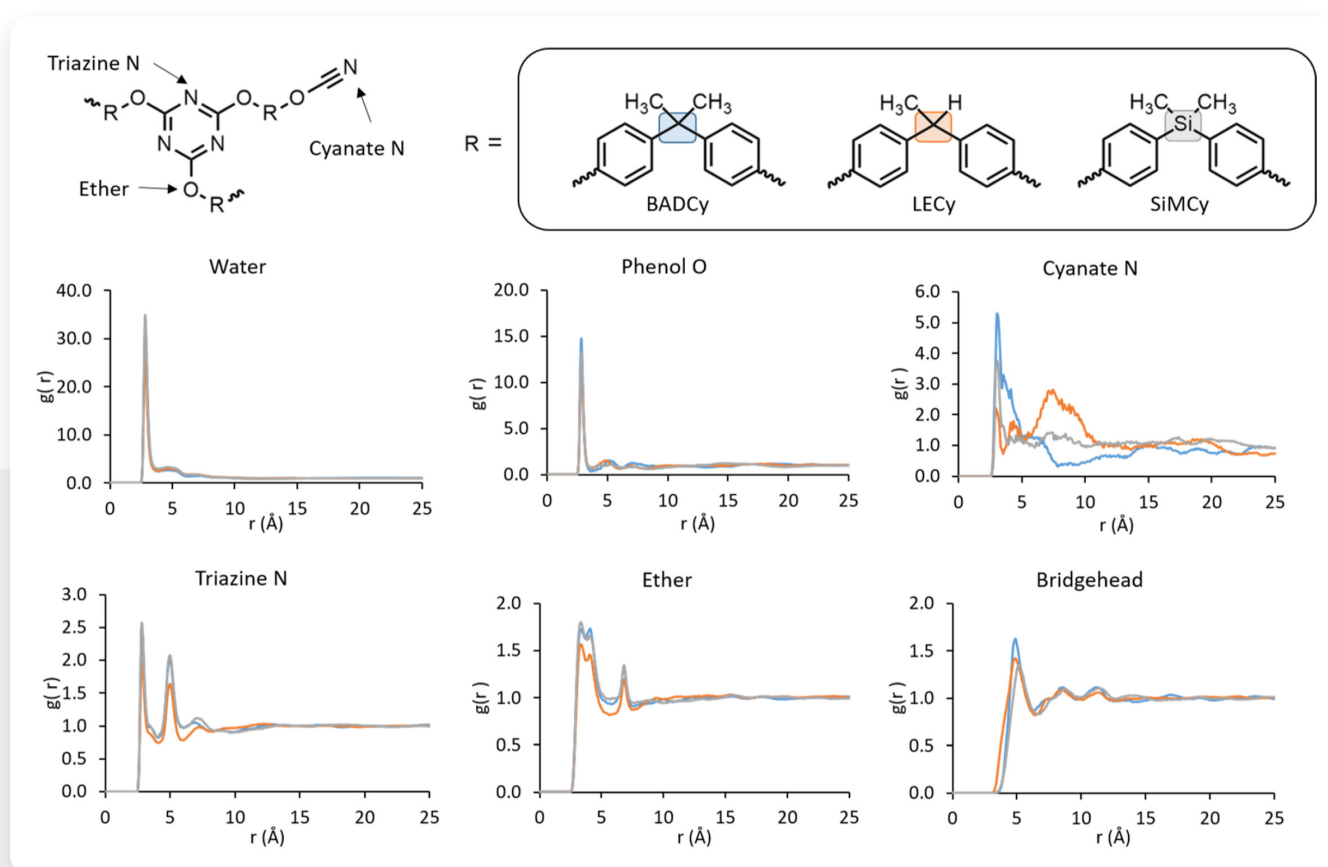
Representative radical distribution functions (RDFs) of water relative to the described moieties in the crosslinked networks. Curves corresponding to BADCy are in blue, LECy in orange, and SiMCy in gray. Note that the y-axes are not all at the same scale.*

References

1. Polycyanurates via Molecular Dynamics: In Situ Crosslinking from Di(Cyanate Ester) Resins and Model Validation through Comparison to Experiment

    Levi M. J. Moore, Neil D. Redeker, Andrea R. Browning, Jeffrey M. Sanders, and Kamran B. Ghiassi, *Macromolecules* 2021, 54, 13, 6275–6284

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