Electronic Supplementary Material (ESI) for Soft Matter.


**Supporting information for**

# Accurate Predictions of Thermoset Resin Glass Transition Temperatures from All-Atom Molecular Dynamics Simulation

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## 1. MD simulation details

The following details provide basic information on the MD simulations of all three thermosetting systems.

*Table S1 - MD simulation parameters for model building, densification, annealing, and equilibration*

| Simulation parameter | Epoxy | PBZ |
|---|---|---|
| Monomers | 260 DGEBF<br>130 DETDA | 256 Benzoxazine |
| Total number of atoms | 15,210 | 14,040 |
| Target mass density | 1.20 g/cc | 1.20 g/cc |
| Replicates | 5 | 5 |
| Glassy build temperature | 300 K | 300 K |
| Rubbery build temperature | 450 K | 473 K |
| Densification simulation time (time steps) | 8 ns (1 fs) | 8 ns (1 fs) |
| Annealing temperature | 600 K | 600 K |
| Annealing ramp rate | -75 K/ns | -50 K/ns |
| Equilibration time (time steps) | 1 ns (1 fs) | 1 ns (1 fs) |

*Table S2 - MD simulation parameters for model crosslinking and final equilibration*

| Simulation parameter | Epoxy | PBZ |
|---|---|---|
| Crosslinking simulation time (time steps) | 8 ns (0.1 fs) | 7 ns (0.1 fs) |
| Average crosslink density | 92% | 70% |
| Equilibration simulation time (time steps) | 1 ns (1 fs) | 1 ns (1 fs) |

*Table S3 - MD simulation parameters for thermal and mechanical property calculations*

| Simulation parameter | Epoxy | PBZ |
|---|---|---|
| Temperature range | 250 – 650 K | 250 – 650 K |
| Heating rate | 50 K/ns | 50 K/ns |
| Cooling rate | -50 K/ns | -50 K/ns |
| Shear strain | 10% | 20% |
| Shear strain rate (time steps) | $2\times10^{8}$ $s^{-1}$ (1 fs) | $2\times10^{8}$ $s^{-1}$ (1 fs) |

Figure S1 shows a representative mass density plot vs simulation time. The window in which the average values of the mass density were calculated (final 500 ps) is shown in the figure. The scatter in the averaging window is incorporated into the predicted mass density values shown in Table 2 of the main manuscript.

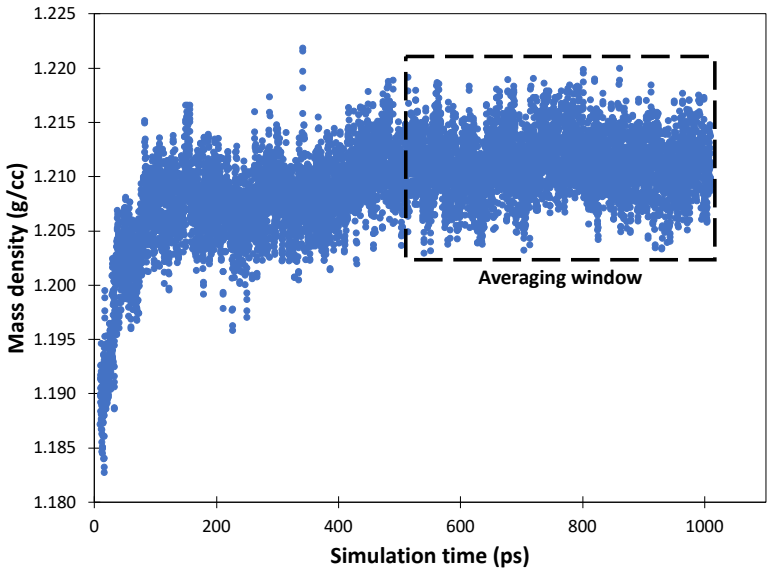


*Figure S1 – Representative mass density vs simulation time plot for an epoxy system.*

Figure S2 shows a representative MD model of the epoxy system.

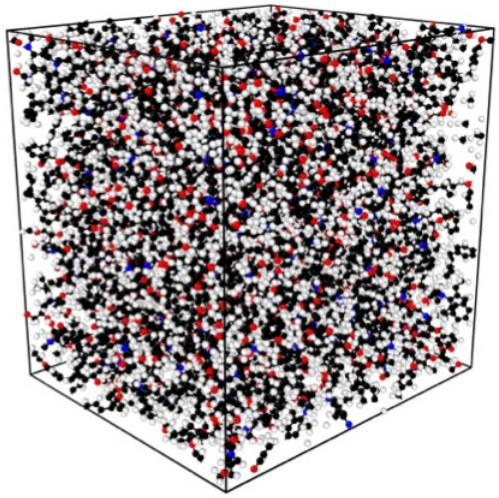

*Figure S2 – Representative MD models of the polymer systems*

Figure S3 shows the mass density and volume regression for a representative epoxy system. The figure also illustrates how the CTE values are determined from the data.

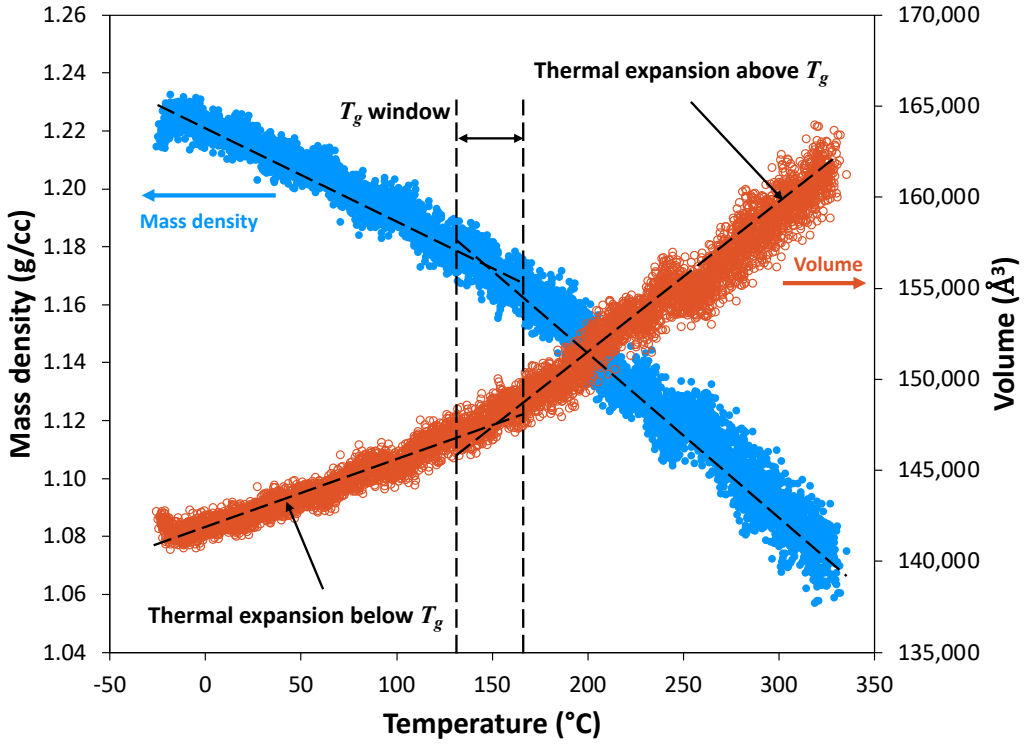


*Figure S3 – Representative mass density and simulation box volume of epoxy as a function of temperature.*

## 2. Simulation results

Tables S4 and S5 show the bulk and shear modulus predictions, respectively, for the epoxy and PBZ systems for two different temperatures. For PBZ, the values are consistently higher for the glassy-build systems, whereas for the epoxy system the difference is not significant. These trends follow that of the mass density (Table 2).

*Table S4 – Predicted bulk modulus*

| Material | Temperature (K) | Glassy build bulk modulus (GPa) | Rubbery build bulk modulus (GPa) |
|---|---|---|---|
| Epoxy | 300 | 6.13 ± 0.24 | 6.12 ± 0.14 |
| | 450 | 4.72 ± 0.25 | 4.57 ± 0.09 |
| PBZ | 300 | 6.02 ± 0.07 | 5.88 ± 0.14 |
| | 473 | 5.53 ± 0.17 | 4.66 ± 0.12 |

*Table S5 – Predicted shear modulus*

| Material | Temperature (K) | Glassy build shear modulus (GPa) | Rubbery build shear modulus (GPa) |
|---|---|---|---|
| Epoxy | 300 | 1.17 ± 0.29 | 1.08 ± 0.25 |
| | 450 | 0.78 ± 0.24 | 0.70 ± 0.25 |
| PBZ | 300 | 2.03 ± 0.04 | 1.63 ± 0.15 |
| | 473 | 1.03 ± 0.16 | 0.87 ± 0.13 |

Table S6 shows the Poisson's ratio predictions for the epoxy and PBZ systems for two temperatures. From the data, there is no statistically significant effect of temperature and build temperature on the predicted Poisson's ratio of both systems.

*Table S6 – Predicted Poisson's ratio*

| Material | Temperature (K) | Glassy build Poisson's ratio | Rubbery build Poisson's ratio |
|---|---|---|---|
| Epoxy | 300 | 0.41 ± 0.02 | 0.42 ± 0.02 |
| | 450 | 0.42 ± 0.02 | 0.42 ± 0.03 |
| PBZ | 300 | 0.34 ± 0.01 | 0.37 ± 0.11 |
| | 473 | 0.41 ± 0.12 | 0.41 ± 0.10 |

## 3. Statistical analysis of replicates

To gain insight into the statistical scatter of predicted properties, the method of Stukowski [1] was used to determine the free volume of the glassy build crosslinked replicate models using a probe size of 1.1 Å. The results of this analysis are provided in Figure S4. It is important to note that the free volume only varied by about 0.02% between the replicates, which is very small. Thus, it is no surprise that there is not a clear dependency of the mass density and Young's

modulus on the free volume. Thus, the variation in the free volume of the models is not responsible for the standard deviations observed between replicates.

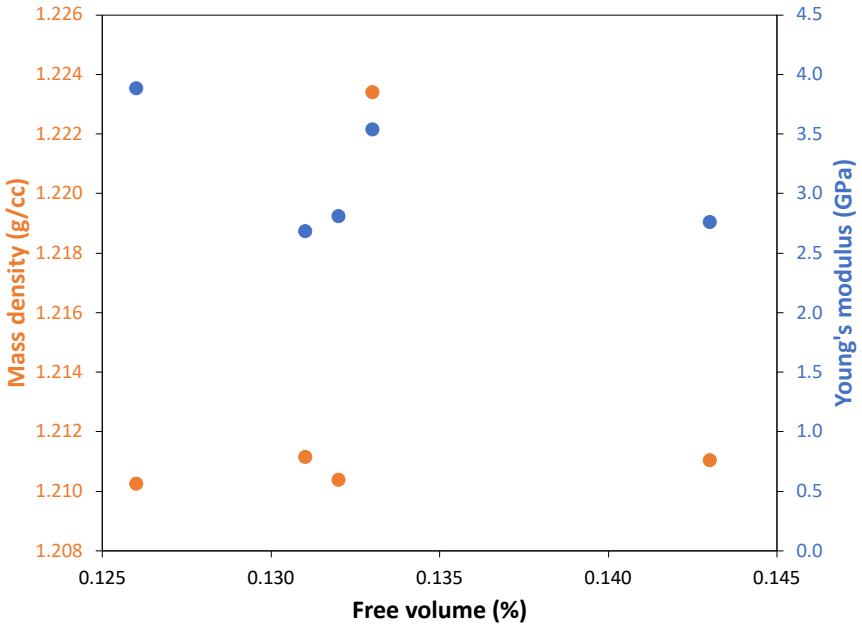


*Figure S4 – Relationship between replicate free volumes, mass densities, and predicted Young's moduli*

The most likely source of the variations in predicted properties between replicates is the morphological differences in the network structure between replicates. Because each replicate was independently built (using identical crosslinking procedures) and these systems are amorphous, the molecular structures between replicates are completely different, and the corresponding crosslinked network structure is expected to be different. It is expected that different network structures can yield different mechanical responses to external loads, even though they have similar mass densities and free volume concentrations.

Zhao et al. [2] previously reported the dependence of system size on the predicted Young's modulus of various epoxy systems. Careful examination of their results show that the average predicted modulus and the corresponding variance does not change significantly for MD model sizes above 17,000 atoms. Because the system sizes in this study are close to the 17,000-threshold shown by Zhao et al, it is expected that the variations in predicted modulus are not affected by the system size.

**4. Statistical analysis of predicted $T_g$ and CTE and simulated cooling rate**

To determine the effect of simulated cooling rate on predicted thermal properties, the $T_g$, CTE below $T_g$, and CTE above $T_g$ values for the epoxy system were predicted for two different cooling rates: 50 K/ns (results reporting in the main document) and 75 K/ns. The resulting predicted thermal properties are summarized in Table S7. The results for both $T_g$ and CTE indicate that there is no statistical difference in predicted values for the two different cooling rates. Even if there is a cooling rate effect in predicted properties from MD simulation, the effect

is too small to be discernible for a range of typical simulated cooling rates. Of course, slower cooling rates could be potentially simulated (1 K/s). However, such simulations would be prohibitively time-consuming.

*Table S7 – Predicted $T_g$ and CTE values for different cooling rates*

| **Property** | **50 K/ns** | **75 K/ns** |
|---|---|---|
| $T_g$ **(°C)** | 144.6 ± 5.7 | 146.1 ± 3.2 |
| **CTE below $T_g$ ($\times 10^{-5}$ °C$^{-1}$)** | 8.8 ± 0.6 | 9.31 ± 0.94 |
| **CTE above $T_g$ ($\times 10^{-5}$ °C$^{-1}$)** | 16.2 ± 0.9 | 15.9 ± 1.2 |

## References


1. Stukowski, A., *Computational Analysis Methods in Atomistic Modeling of Crystals.* JOM, 2014. **66**(3): p. 399-407.
2. Zhao, Y., G. Kikugawa, Y. Kawagoe, K. Shirasu, N. Kishimoto, Y. Xi, and T. Okabe, *Uncovering the Mechanism of Size Effect on the Thermomechanical Properties of Highly Cross-Linked Epoxy Resins.* The Journal of Physical Chemistry B, 2022. **126**(13): p. 2593-2607.