Supplementary Information for

Exploring secondary interactions and the role of temperature in moisture-contaminated polymer networks through molecular simulations

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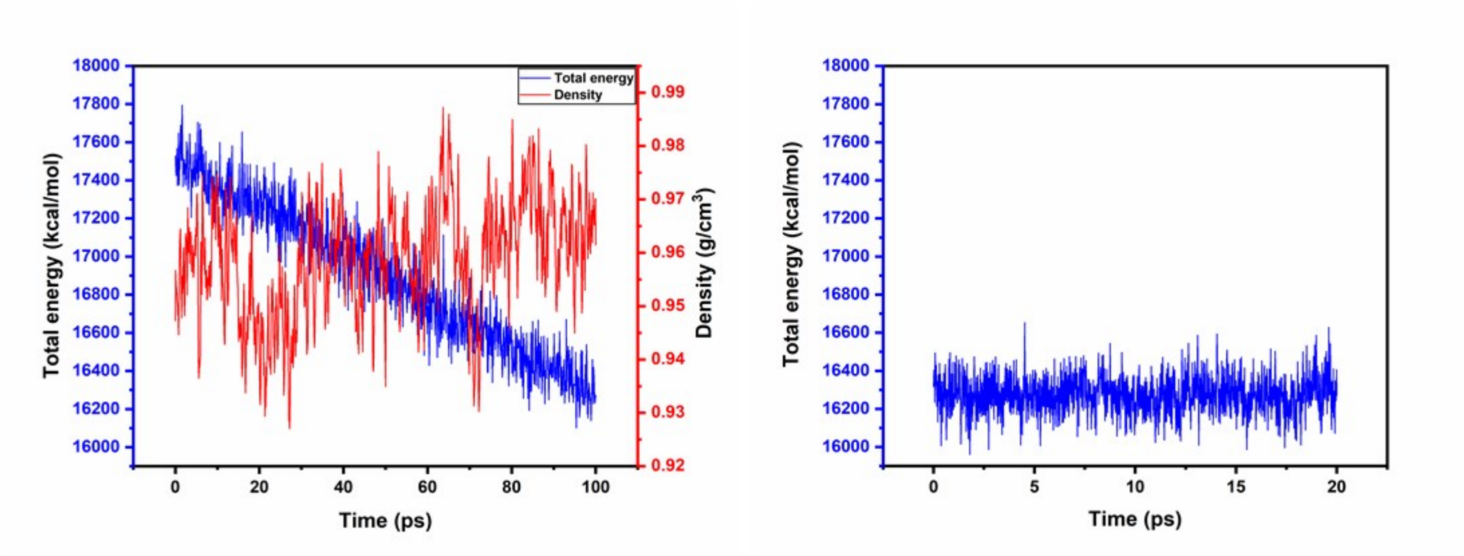
Simulation Details

1. **Annealing and Equilibration Cycle:** As illustrated in Figure S1 (a), the total energy of the system decreased with temperature during the 100 ps simulation. In the same simulation period, there was a gradual but steady rise in the system density— indicating that the volume of the system decreased as the system relaxed. During the short, fixed-temperature equilibration run the total energy fluctuated about a mean, as observed in Figure S1 (b).



(a) (b)

Figure S1: Evolution of - a) Total energy and density in an annealing cycle b.) Total energy in subsequent equilibration cycle

A total of six annealing and seven equilibration cycles were performed as the temperature decreased from 600K to 300K. The extra equilibration cycle was performed at 600K before the first annealing cycle. The data in Figure S1 (a) and (b) is from the second annealing and third equilibration cycle of the 81% crosslinked system, respectively. The final density achieved by both the epoxy networks was ~1.05 g/cm^3, which is consistent with previous results.

2. **Glass Transition Temperature (T_g) of epoxy matrices:** After a 100-step geometry

optimization, 300 ps NPT simulations at 1 atm were conducted at specific temperatures ranging from 500 to 200 K. The temperature was lowered by 30 K after each step and a short 50 ps NVT simulation was conducted to equilibrate the systems before starting the NPT simulations at a particular temperature. Therefore, a total of 10 simulations were performed at decreasing temperatures and the mean density (**ρ**) was calculated at every step. Subsequently the specific volume $(1/\rho)$ was plotted as a function of temperature and the T_g was calculated by finding the point where the slope of the curves between the rubbery and the glassy states intersect. The results have been compiled in Figure S2 and as expected, the T_g decreases significantly with decreasing crosslinking. We observe that the T_g is ~380 K for the network with higher crosslinking density while it drops to ~ 325 K for the 20% crosslinked network. These results are remarkably consistent with previous simulation studies which have reported T_g values of 378 K [1] and 384 K [2] respectively for highly crosslinked systems. These values are slightly higher than the reported experimental values of ~360 K [3; 4] for DGEBA based epoxies, and the difference can be due to the prolonged cure schedule in an experimental scenario when compared to the faster cooling rates in molecular simulations.

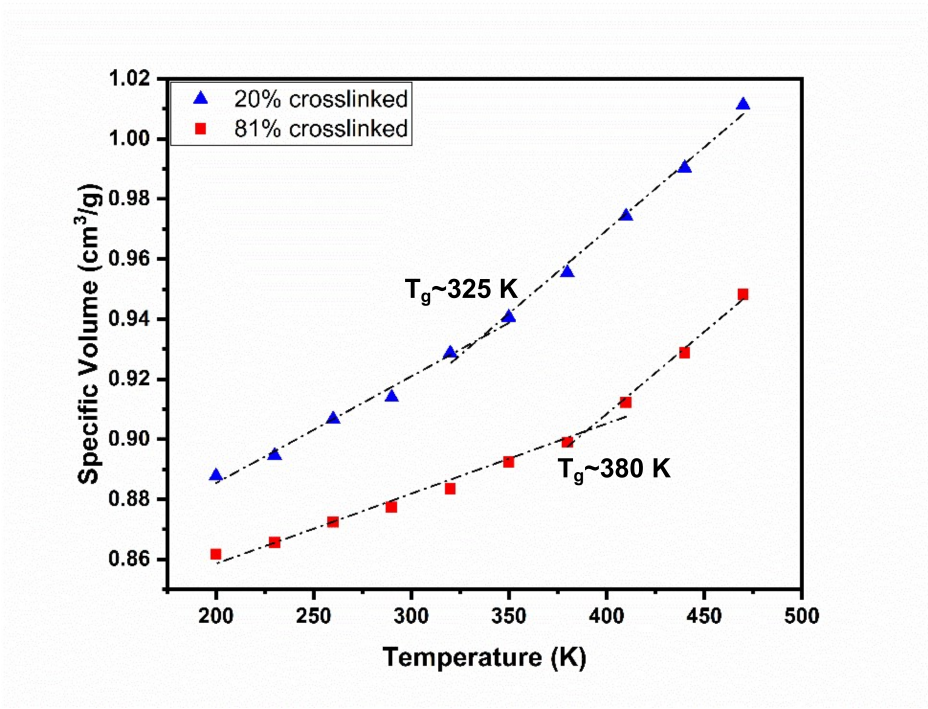


Figure S2: Temperature variation of specific volume at different crosslinking densities.

3.

3.1 Radial Distribution Function: A correct interpretation of the RDF plot reveals details about the atomic structure of the system being simulated. If the sets of atoms in consideration are unstructured and do not have any correlation with each other, the RDF plot is flat, indicating that there is equal probability of finding another particle at a distance "r" which is well-demonstrated in Fig. S3 beyond 4 Å. In an amorphous system like a crosslinked polymer network, this smoothing is also evidence of the lack of long-range order. As the system becomes increasingly ordered, the interparticle distance becomes more defined and we can see sharp peaks in the RDF plot signifying higher probability of finding another particle at some particularly favored separation distance, which is the case in a liquid or solid system [Fig S3].

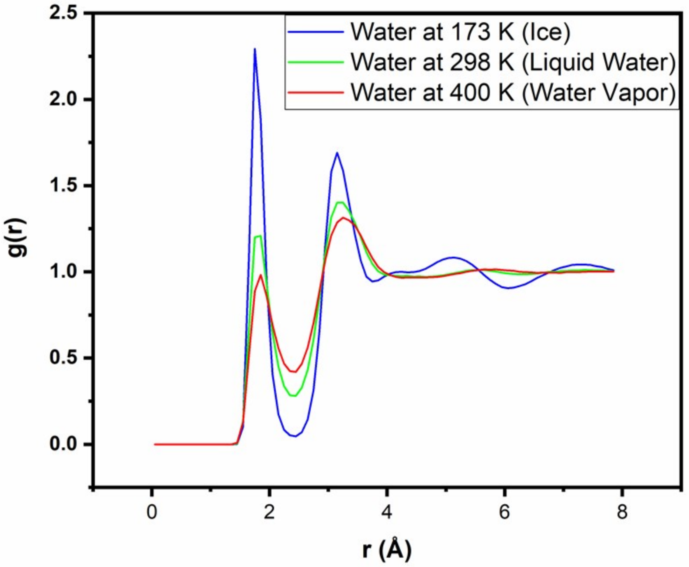


Figure S3: The intermolecular radial distribution functions between oxygen (Ow) and Hydrogen (Hw) for water at different temperatures

3.2 RDF between polar nitrogen and water molecules in epoxy network: As seen in Figure S4 (a) and (b), for the Ow-N g(r) curves, a very small shoulder is observed at ~3 Å and a broader peak is seen at ~5 Å. This indicates that van der Waals and electrostatic interactions dominate in the nitrogen-water polar pair. The peak magnitudes are consistently lower when compared to the Ow-OH RDF peaks for both crosslinking densities, and they reduce with increasing temperatures, similar to the other RDF curves. The peaks for the 20% crosslinked network are particularly low and they quickly flatten out at increasing temperatures. We suspect that this is due to the small size of the hardener molecule (DETA) which contains the nitrogen sites. When the crosslinking density is as low as 20%, we have a large population of these small, uncrosslinked hardener molecules and as the thermal energy of the system increases, both the water molecules and the DETA molecules will have very high mobility making it less likely for them to engage in any form of secondary bonding interactions.

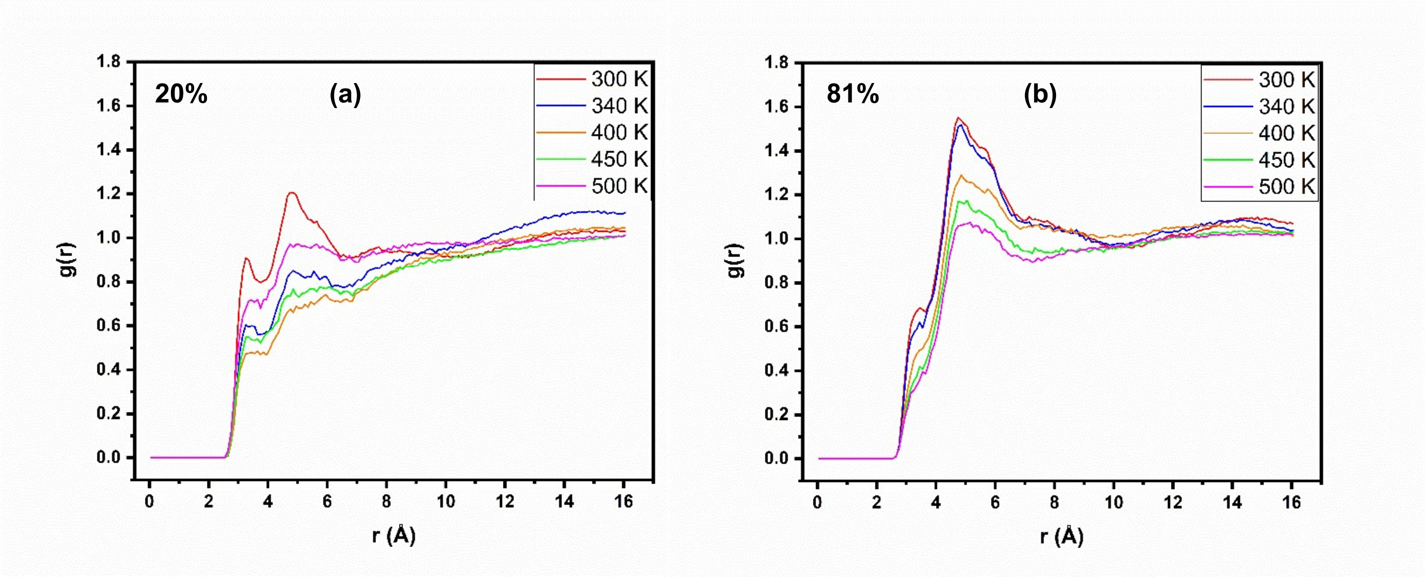


Figure S4: Intermolecular RDF between the oxygen of the water molecules (Ow) and the polar nitrogen (N) for (a.) 20% crosslinked network and (b.) 80% crosslinked network

Table S1: Partial charges assigned to all polar atoms in polymer network.

Polar Species	**Description**	**Partial Charge**
Ow	Oxygen in water molecule	-0.8300
Hw	Hydrogen in water molecule	+0.4150
OH	Oxygen in Hydroxyl group of epoxy	-0.3882
HO	Hydrogen in Hydroxyl group of epoxy	+0.2099
Oe	Oxygen in Ether group of epoxy	-0.3421
Ou	Oxygen in unreacted ring of epoxy	-0.3694
N1	Primary Nitrogen atom in hardener	-0.3283
H1	Hydrogen atom connected to Primary Nitrogen	+0.1183
N2	Secondary Nitrogen atom in hardener	-0.3136
H2	Hydrogen atom connected to Secondary Nitrogen	+0.1220
N3	Tertiary Nitrogen atom in hardener	-0.2961

4. Mean Square Displacement (MSD).

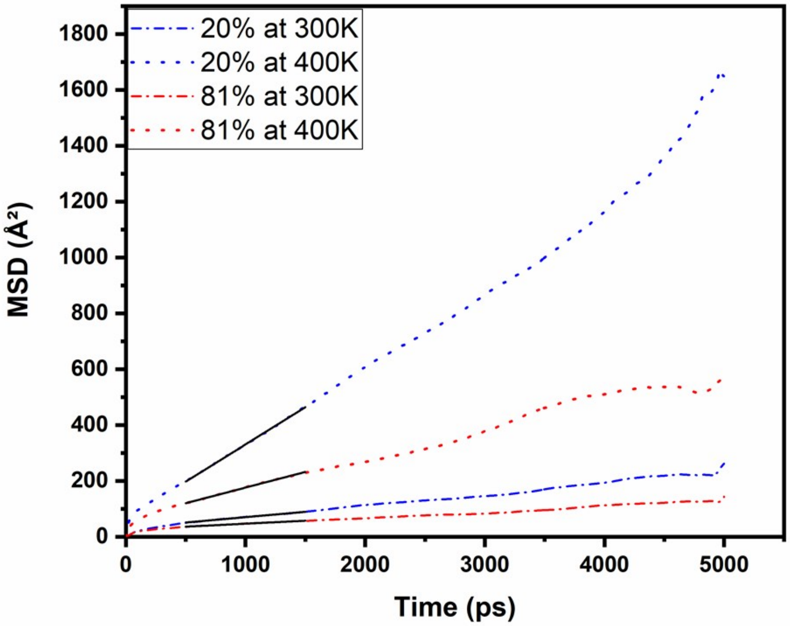


Figure S5: MSD of water molecules in the two networks as a function of temperature

Figure S5 illustrates that as temperature increases the MSD of the water molecules increase by orders of magnitude due to the increased thermal energy available in the system. The best time period of sufficient duration (~1 ns) where all the curves are reasonably linear is between 500-1500 ps (shown by black solid line) and this window was chosen for applying eqn. (ii) to calculate the diffusion coefficient (D).

References

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