

COLVARS-Driven Reactive Molecular Dynamics of Vitrimer Polymerization and Thermomechanical Property Analysis

Yajan Adhikari¹, Ujjawal Chapagai¹, Sushan Khanal¹

1. Reformix AI

Abstract

Vitrimers are the new class of covalent adaptable networks (CANs) capable of topological rearrangement through dynamic bond exchange, enabling recyclability, self-healing and stress relaxation while maintaining network integrity. The ring opening of epoxides by carboxylic acids is a fundamental epoxy–acid esterification reaction underlying vitrimer network formation, yet its atomistic mechanism remains challenging to simulate as experimental time scales for crosslinking reactions in polymers range from minutes to hours—far beyond the reach of atomistic molecular dynamics (MD) simulations. In this work, we employ biased MD using the Collective Variables (COLVARS) module in LAMMPS combined with a reactive ReaxFF potential to promote the ring-opening reaction between Diglycidyl Ether of Bisphenol A (DGEBA) and oxalic acid. Three coupled collective variables were designed to represent epoxide C–O bond cleavage, C(epoxide)–O(acid) bond formation, and proton transfer between acid and epoxide oxygens. This external bias promotes nucleophilic addition of acid-derived carboxylate oxygen to the epoxide carbon, resulting in ring opening, followed by proton transfer to yield the β -hydroxy ester functionality characteristic of vitrimer networks. This method allows simulating cross-linking at realistic, low, temperatures which helps to mimic chemical reactions and avoids unwanted high-temperature side reactions. Since not all accelerated events lead to the desired product, careful selection of initial configurations, molecular orientations, and suitable external bias parameters increases the probability of meaningful simulation results. Furthermore, the stability of the resulting vitrimer was evaluated in the absence of any external bias, and its thermomechanical properties were subsequently analyzed. Results show that the biased MD approach successfully captures the atomistic steps of the esterification reaction and the resulting vitrimer network can be used for accurate prediction of thermomechanical properties.

Keywords

Vitrimers, Covalent adaptable networks, Reactive molecular dynamics, COLVARS, ReaxFF, Epoxide ring-opening, Thermomechanical properties, Polymer crosslinking

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Vitrimers are the new class of covalent adaptable networks (CANs) capable of topological rearrangement through dynamic bond exchange, enabling recyclability, self-healing and stress relaxation while maintaining network integrity. The ring-opening of epoxides by carboxylic acids is a fundamental epoxy–acid esterification reaction underlying vitrimer network formation, yet its atomistic mechanism remains challenging to simulate as experimental time scales for crosslinking reactions in polymers range from minutes to hours—far beyond the reach of atomistic molecular dynamics (MD) simulations. In this work, we employ biased MD using the Collective Variables (COLVARS) module in *LAMMPS* combined with a reactive ReaxFF potential to promote the ring-opening reaction between Diglycidyl Ether of Bisphenol A (DGEBA) and oxalic acid. Three coupled collective variables were designed to represent epoxide C–O bond cleavage, C(epoxide)–O(acid) bond formation, and proton transfer between acid and epoxide oxygens. This external bias promotes nucleophilic addition of acid-derived carboxylate oxygen to the epoxide carbon, resulting in ring opening, followed by proton transfer to yield the β -hydroxy ester functionality characteristic of vitrimer networks. This method allows simulating cross-linking at realistic, low, temperatures which helps to mimic chemical reactions and avoids unwanted high-temperature side reactions. Since not all accelerated events lead to the desired product, careful selection of initial configurations, molecular orientations, and suitable external bias parameters increases the probability of meaningful simulation results. Furthermore, the stability of the resulting vitrimer was evaluated in the absence of any external bias, and its thermomechanical properties were subsequently analyzed. Results show that the biased MD approach successfully captures the atomistic steps of the esterification reaction and the resulting vitrimer network can be used for accurate prediction of thermomechanical properties.

1) Introduction

Plastics are versatile polymeric materials composed of long-chain macromolecules that can be shaped and solidified into durable forms. Based on the molecular arrangement of their chains, plastics can be divided into two main categories, namely thermoplastics and thermosetting plastics [1]. Thermoplastics consist of linear or branched polymer chains held together by weak intermolecular forces, allowing them to soften upon heating and harden upon cooling. This reversible process allows them to be recycled and remolded multiple times. In contrast, thermosetting plastics form extensive covalent crosslinking during curing, providing them with

excellent mechanical strength, chemical stability and heat resistance. However, once molded, these permanent covalent bonds prevent thermosets from being reprocessed or repaired, leading to significant challenges in recycling and end-of-life management [1], [2]. Hence, it is of significant scientific interest to develop a high-performance, recyclable polymer that combines the mechanical robustness of thermosets with the reprocessability of thermoplastics. This process led to the emergence of covalent adaptable networks (CANs) — polymeric systems that incorporate dynamic covalent bonds capable of reversible exchange under specific stimuli such as heat, light, or chemical catalysis [3]. Among CANs, vitrimers represent a distinct subclass that undergoes topological rearrangement via associative bond-exchange reactions. First characterized by Leibler and colleagues in 2011, vitrimers maintain network integrity during bond rearrangement, allowing the material to flow like a viscoelastic liquid at elevated temperatures while preserving the overall number of covalent bonds [4], [5]. This unique mechanism imparts vitrimers with exceptional reprocessability [6a], self-healing [6b], and stress-relaxation capabilities [6c], all while retaining mechanical strength and dimensional stability under service conditions.

Understanding and optimizing vitrimer behavior requires an atomistic approach of the structural rearrangements and reaction pathways that dictate their macroscopic properties. In this context, molecular dynamics (MD) simulations have emerged as a powerful tool to bridge this gap by providing detailed insight into the motion, interactions, and transformations of atoms over time [7], [8]. However, accurately simulating the crosslinking process in vitrimer systems also remains challenging, as the reaction timescales observed experimentally—typically ranging from several minutes to hours—greatly exceed those accessible by atomistic molecular dynamics simulations. Previous studies have employed several computational strategies to overcome this limitation and model polymer crosslinking. Coarse-grained molecular simulations simplify the system by representing groups of atoms as beads, sacrificing atomistic detail for computational efficiency [8-10]. At the atomic level, distance-based crosslinking methods have been widely used, where bonds are formed once reactive sites fall within a predefined cutoff distance [11-14]. While these approaches enable the construction of crosslinked networks, they often neglect the effects of molecular geometry and steric hindrance, and the resulting reactions may not accurately reflect the true chemical mechanisms of polymerization.

Building on these previous approaches, the method presented in this work overcomes several key limitations of existing simulations. Unlike coarse-grained simulations, our approach preserves full atomistic detail, allowing for an accurate representation of both the molecular geometry and steric effects during crosslinking. Compared to traditional distance-based methods, which rely solely on proximity criteria to form bonds, we employ biased molecular dynamics using the COLVARS module [15] in LAMMPS combined with a reactive ReaxFF force field [16]. This approach enables the selective promotion of specific chemical reactions, such as the ring-opening of epoxides by carboxylic acids, by explicitly controlling bond distances and proton transfer events through well-defined collective variables [15]. By coupling multiple collective

variables—representing epoxide C–O bond cleavage, C(epoxide)–O(acid) bond formation, and proton transfer—the methodology captures the sequential chemical steps of the reaction pathway encompassing reactants, transition state and product, rather than forming bonds arbitrarily when atoms are close. This ensures that steric hindrance, orientation effects, and reaction energetics are properly considered, resulting in a chemically realistic simulation of polymerization. Moreover, the use of external bias allows reactions to occur at experimentally relevant low temperatures, minimizing artificial high-temperature side reactions and enabling the study of crosslinking under conditions that closely mimic real experimental scenarios.

2) Materials and Methods

DGEBA (Diglycidyl Ether of Bisphenol A) and oxalic acid [fig. 1] were selected as representative molecular systems. The molecular structures of DGEBA and oxalic acid were obtained from the PubChem database [17a, 17b]. DGEBA was chosen as a model epoxy precursor due to its widespread application in thermosetting and vitrimeric epoxy networks. Although oxalic acid is not commonly used in vitrimer formulations because of its volatility and limited capability to form extended crosslinked structures, it was employed here as a model carboxylic acid owing to its simple structure and well-defined reactive sites, enabling clear mechanistic characterization of the epoxide ring-opening and esterification process.

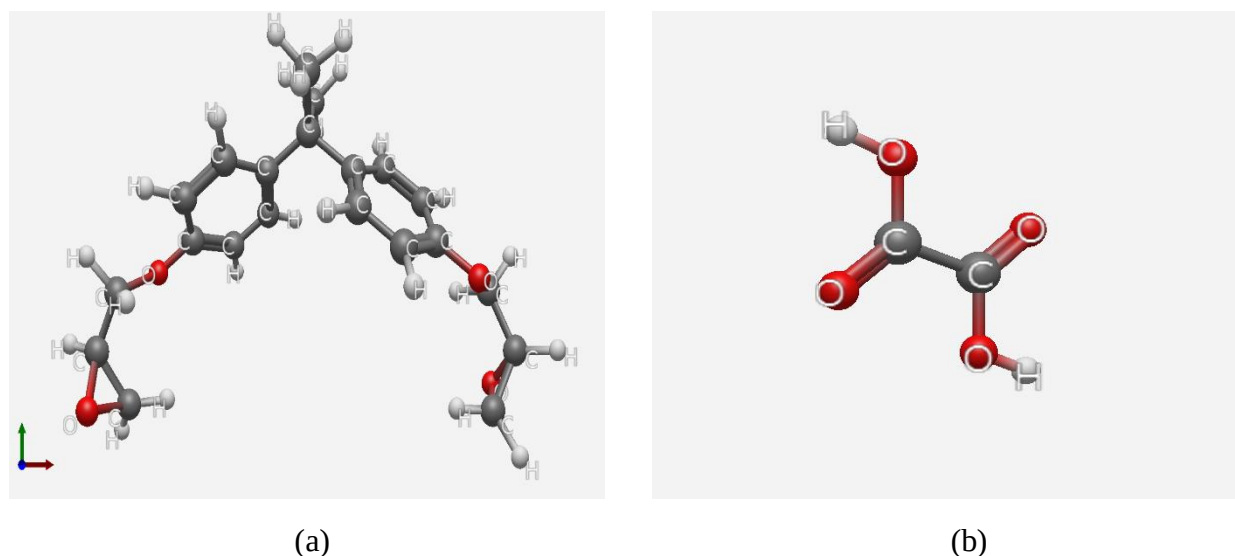


Figure 1: Representative molecules used to model large-scale polymerization, (a) Diglycidyl Ether of Bisphenol A (DGEBA), (b) oxalic acid. Grey, red and white respectively represent carbon, oxygen and hydrogen (marked in picture also for ease)

The epoxide ring opening by dicarboxylic acids proceeds via a nucleophilic addition mechanism. Carboxylate nucleophile attacks the less substituted carbon of the epoxide ring, leading to ring

opening and formation of a β -hydroxy ester linkage. This stepwise process involves proton transfer and is not strictly concerted but exhibits SN2 like regioselectivity. The resulting β -hydroxy ester groups enable subsequent transesterification reactions characteristic of vitrimer networks. This reaction mechanism is shown in Figure 2.

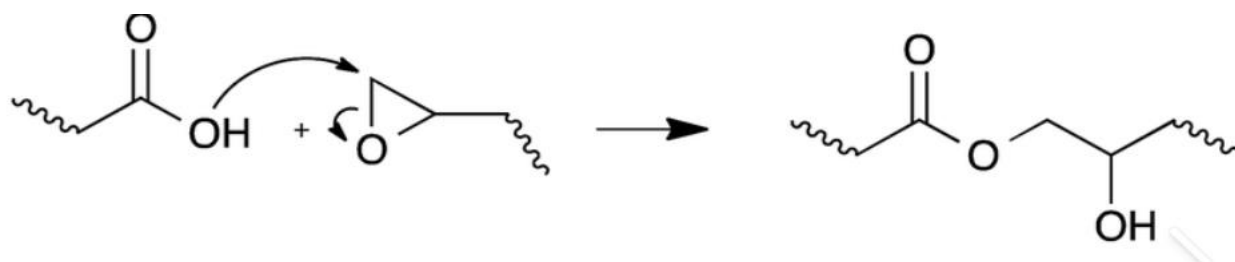


Figure 2: Schematic representation of the reaction mechanism between an epoxy group and a carboxylic acid. The nucleophilic oxygen of the -COOH group attacks the electrophilic carbon of the epoxide ring, leading to ring opening and formation of a β -hydroxy ester

All reacting molecular geometries were pre-optimized using density functional theory (DFT) with the B3LYP functional and the def2-SVP basis set in ORCA [18–21]. Optimizations were carried out in the gas phase without solvent or environmental effects to ensure that the computed geometries and energies reflect intrinsic molecular reactivity. These well-converged structures served as starting points for subsequent polymerization.

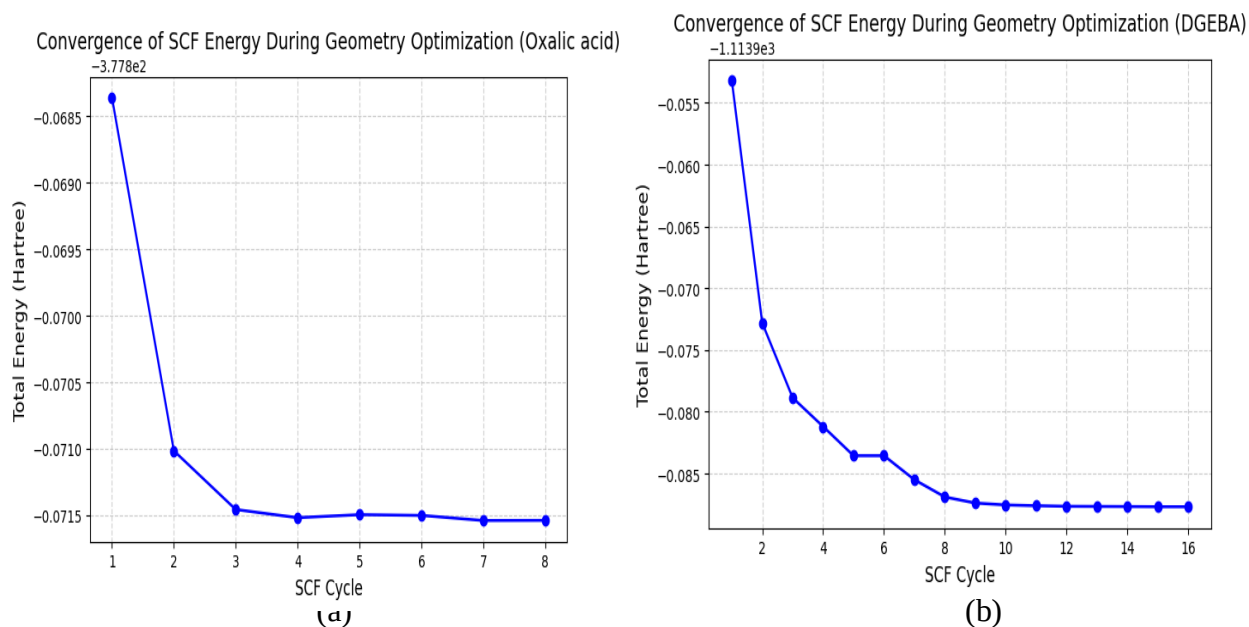


Figure 3: Convergence of the self-consistent field (SCF) energy during the geometry optimization of the molecule (a) oxalic acid, (b) DGEBA. The plot shows the total electronic energy (in Hartree) as a function of SCF iteration number, demonstrating that the energy steadily decreases and converges to a stable minimum, indicating a well-optimized molecular structure.

2.1. Computational Details

Reactive molecular dynamics (MD) simulations were carried out using LAMMPS [22] with the ReaxFF reactive force field CHNO-2017_weak force field modified by Vashith et al to describe the interactions among carbon, hydrogen, and oxygen atoms [23]. Partial atomic charges were updated at every timestep through the charge equilibration scheme (fix qeq/reax) to account for dynamic charge redistribution during bond formation and breaking. Initial system consisted of a well-equilibrated structure of DGEBA, and oxalic acid placed in periodic simulation box as shown in fig. 4.

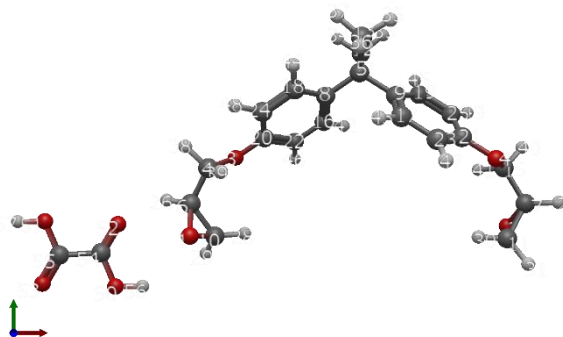


Figure 4: Starting geometry for first polymerization step.

To accelerate the ring-opening event, a collective variable (COLVAR) [15] was applied on the interatomic distances—namely C_{ep}–O_{ep} (epoxide bond), C_{ep}–O_{acid} (new bond), and O_{acid}–H (proton transfer). Each of these coordinates was treated as a separate collective variable (CV) and biased using harmonic potentials within the Colvars module of LAMMPS to steer the system along the desired reaction pathway. For a given collective variable ξ , the biasing potential applied during the simulation is described by a harmonic restraint of the form:

$$V_{\text{bias}}(\xi) = \frac{1}{2}k[\xi - \xi_0(t)]^2 \dots \quad (1)$$

where k is the force constant, ξ is the instantaneous value of the CV, and $\xi_0(t)$ is its time-dependent target value. The latter was linearly ramped from an initial to a final value over the course of the molecular dynamics simulation to ensure a gradual and physically meaningful transition along the reaction coordinate:

$$\xi_0(t) = \xi_{\text{initial}} + \left(\frac{\xi_{\text{final}} - \xi_{\text{initial}}}{N_{\text{steps}}} \right) t \dots \quad (2)$$

In addition, harmonic wall potentials were used to confine the CVs within realistic physical limits and to prevent unphysical bond stretching or compression. The wall potential takes the general form:

$$V_{\text{wall}}(\xi) = \frac{1}{2} k_{\text{wall}} (\xi - \xi_{\text{wall}})^2 \quad \dots \quad (3)$$

and is only active when ξ exceeds the predefined wall boundaries.

In this setup, the three collective variables bias the stepwise S_N2-like ring-opening of the epoxide, where nucleophilic attack by the carboxylate oxygen opens the epoxide, followed by proton transfer to form the β -hydroxy ester linkage.

The parameters controlling each collective variable—including the initial and target values of the CVs, force constants, and harmonic wall limits—were carefully chosen, running short preliminary MD test simulations to ensure gradual progression along the desired reaction coordinates without introducing unphysical distortions. A summary of these parameters for each CV is provided in Table 1, which specifies the biasing conditions applied to the epoxide bond cleavage, nucleophilic attack, and proton transfer steps.

Table 1: Parameters used for the collective variables (COLVARS) in the reactive MD simulations. Each CV corresponds to a key reaction coordinate: epoxide C–O bond breaking, C(epoxide)–O(acid) bond formation, and proton transfer. The table lists the initial and target harmonic centers, ramp lengths (number of MD steps), force constants, and harmonic wall limits applied to ensure smooth and physically meaningful transitions along the reaction pathway.

CV Name	Atom Pair (Group1–Group2)	Initial Center (Å)	Target Center (Å)	Force Constant (kcal/mol·Å ²)	Lower Wall (Å)	Lower Wall k	Upper Wall (Å)	Upper Wall k
dist_CO_epoxide	O(epoxide)–C(epoxide)	1.399	2.40	80.0	1.0	5.0	4.5	5.0
dist_CO_acid	C(epoxide)–O(acid)	5.459	1.43	800.0	1.0	5.0	6.5	5.0
d_H_diff	H(acid)–O(epoxide)	5.761	1.1	500.0	-8.0	2.0	8.0	2.0

Note: The parameters listed correspond to the first stage of polymerization involving a single DGEBA and one oxalic acid molecule. These values can be reused for subsequent polymerization stages with minute changes depending on polymer size.

While experimental studies use 1,5,7-triazabicyclo [4,4,0]dec-5-ene (TBD) as a catalyst to regulate exchange reaction rates, our simulations model only the polymerization step and therefore do not include TBD.

The detailed setup of COLVARs input file and output trajectory are provided in supporting information (S.I.) section.

2.2 Polymer builder strategy

Hierarchical multistep approach was employed to build the large polymer network [23]. Initially, one molecule of DGEBA and oxalic acid were put in a system with an approximate density of 0.5-0.7 g/cm³ [fig.4]. Simulations were performed in the NVT ensemble using a Nosé–Hoover thermostat at a temperature of 423 K with a time step of 0.05 fs and thermostat damping 100 fs. Accelerated simulations using the collective variable (Colvars) bias were applied to promote the epoxide ring-opening and subsequent ester linkage formation between the carboxyl and epoxide functional groups.

After successful bond formation in this initial stage, the resulting dimeric unit [Fig. 5] was extracted and optimized using B3LYP functional and the def2-SVP basis set in ORCA [18–21]. The optimized structure was replicated to construct a larger system while maintaining the 1:1 stoichiometric ratio of DGEBA and oxalic acid. The new configuration, with doubled system size and a similar target density ($\approx 0.5\text{--}0.7\text{ g cm}^{-3}$), was subjected again to accelerated NVT simulations at 423 K to allow further crosslinking. This hierarchical assembly process was repeated iteratively, with each step effectively increasing the molecular weight and connectivity of the growing polymer network.

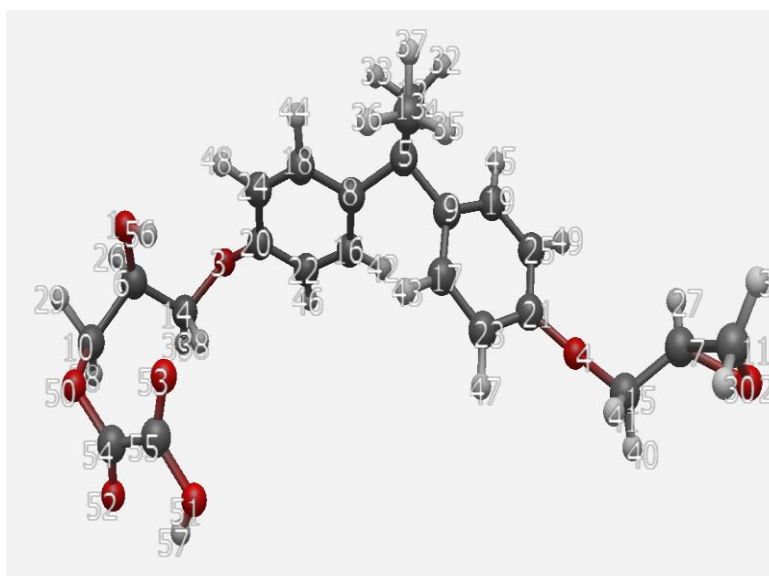


Figure 5: Representative dimeric unit obtained after the initial accelerated simulations of one DGEBA and one oxalic acid molecule, illustrating successful epoxide ring-opening and ester linkage formation.

It should be noted that the probability of bond formation decreases with the growing size of the polymer system as it is difficult to satisfy the configurational requirements for accelerated simulations [23]. Hence, considering the growing complexity of the system, biasing duration was also increased in the subsequent stages to provide smooth potential and prevent abrupt and unphysical movements during the bond formation and cleavage. The final polymer was a long continuous chain made up of 456 atoms—i.e., 8DGEBA and 8oxalic acid molecules.

2.3. Polymer's property analysis

The resulting polymer network exhibits significant local heterogeneity, which results in uneven stress distribution and spatially varying mobility, ultimately reducing mechanical predictability and reproducibility [24]. To mitigate this, a repetitive annealing protocol was applied, following the general procedure of Refs. 23 and 25. In brief, polymer was heated from 300K to 600K and then cooled back to 300K. The temperature increased in 100K increments through NVT ramp, and at each temperature an NPT simulation was performed to allow density to equilibrate. Each NPT and NVT step was run for 12.5ps using a 0.25fs timestep. Berendsen thermostat (100 fs) and barostat (500 fs) damping constants were used. The final annealed structure was used for further analysis of polymer's property.

To determine the room-temperature density, the equilibrated density values from the final NPT segment of the annealing cycle at 300K were used. The time-series of density data from this segment was analyzed using the PyMBAR timeseries module to detect the onset of equilibration and to compute statistical inefficiency [26]. Only the equilibrated portion of the trajectory was used to determine the mean density, and standard error was calculated from the effective number of uncorrelated samples using:

$$SEM = \frac{\sigma}{\sqrt{N_{eff}}} \quad \dots (4)$$

The T_g of the polymer was estimated using **molecular dynamics simulated annealing** with the in LAMMPS. The system was first equilibrated at 300 K under an NPT ensemble, then heated to 450K and subsequently cooled back to 300K in **10 K steps**, with density recorded at each temperature. The T_g was determined from the **inflection point of the density vs. temperature curve**, corresponding to the change in the thermal expansion coefficient. A detailed description of the T_g determination procedure, including spline fitting, derivative analysis, and uncertainty estimation, is provided in the Supporting Information.

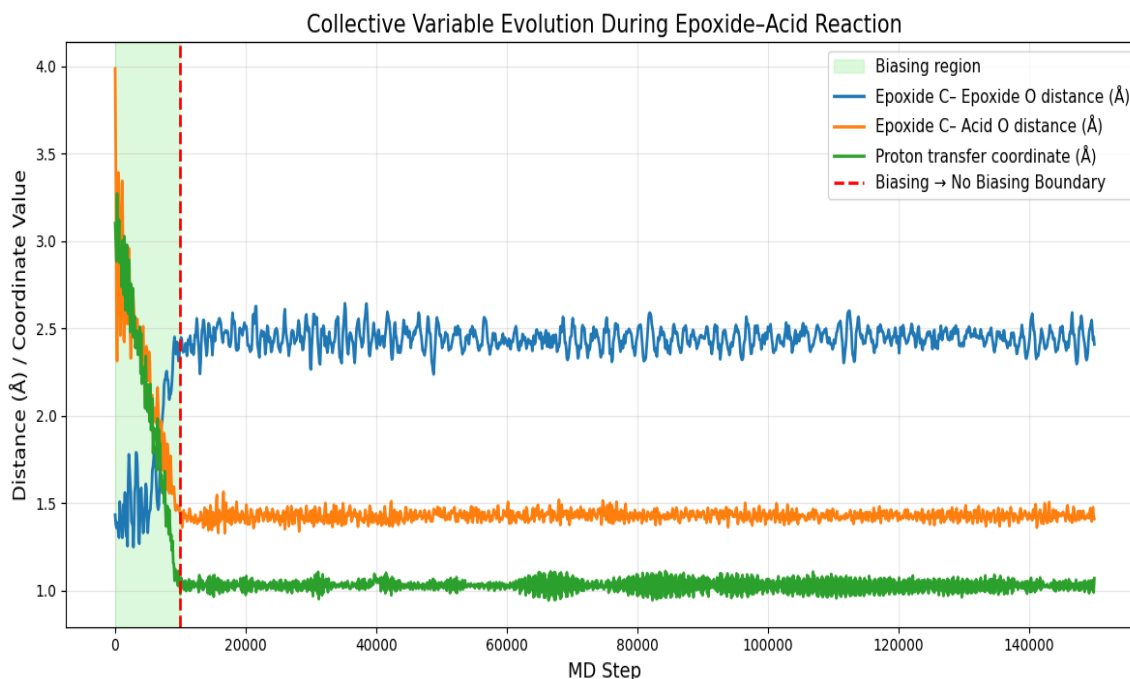
Next, the vitrimer's tensile modulus is predicted using LAMMPS. Since it is challenging to simulate experimental strain rates, we used very high strain rate for simulating uniaxial tensile deformation [27]. The annealed structure was subjected to three uniaxial tensile deformation simulations: tension in the x-, y- and z- directions. The system was deformed incrementally at each timestep, achieving a total engineering strain of 20% within 100ps, corresponding to an effective strain rate of $2 \times 10^9 \text{ s}^{-1}$. A Nose–Hoover barostat was applied in the transverse

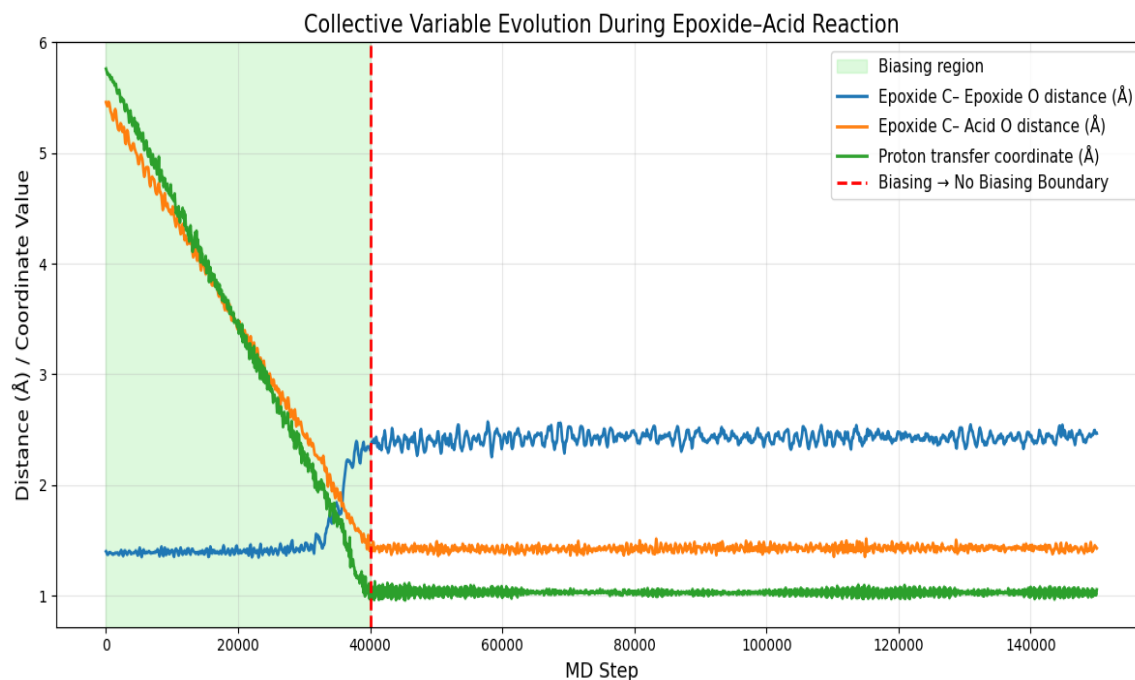
directions to maintain atmospheric pressure and allow natural Poisson contraction. The simulations were carried out at 300 K using a timestep of 0.25 fs.

Results and Discussion

3.1. Validation of Biased Molecular Dynamics and Reaction Mechanism

To ensure that the biased molecular dynamics (MD) simulation accurately captured the epoxide–acid ring-opening process correctly, the evolution of the collective variables (CVs) was analyzed throughout the simulation. Figure 6a, 6b illustrates the time-dependent behavior of the C(epoxide)–O(epoxide), C(epoxide)–O(acid), and proton-transfer coordinates during first and second stage of polymerization respectively. Initially, the C(epoxide)–O(epoxide) bond length(blue) remains near 1.45 Å, while the C(epoxide)–O(acid)distance(orange) exceeds 3.5 Å, indicating an intact epoxide ring and unreacted acid.





(b)

Figure 6: Collective variable evolution during the biased molecular dynamics simulation of the epoxide–acid reaction a) for stage 1 of polymerization b) for stage 2 of polymerization. The shaded region indicates the biasing interval, and the red dashed line marks the transition to unbiased dynamics. Stabilization of the collective variables beyond the biasing boundary confirms successful ring opening and ester formation.

When the biasing potential is applied (shown by shaded region), the carboxylate nucleophile of acid (orange) steadily moves closer to the carbon of epoxide. The epoxide C–O bond (blue) stays almost unchanged until the carboxylate nucleophile of acid reaches about **1.6 Å**, where the acid's oxygen interacts with the strained bond and ring begins to open. Concurrently, the proton-transfer coordinate decreases to ~ 1.0 Å, indicating hydrogen transfer from the acid to the less hindered epoxide oxygen as the new C–O bond forms.

Beyond the biasing region (past the red dashed line), all collective variables showed minimal fluctuations, confirming the product's structural stability without external bias. The observed evolution of interatomic distances is consistent with an S_N2 -like nucleophilic addition mechanism, in which an acid-derived carboxylate oxygen attacks the electrophilic epoxide carbon. The simultaneous elongation of the epoxide C–O bond and shortening of the C(epoxide)–O(acid) distance reflects the progression of epoxide ring opening, followed by proton transfer, leading to formation of the β -hydroxy ester linkage characteristic of vitrimer networks.

To further validate the accuracy of biased MD trajectory, snapshot corresponding to transition state is represented in fig. 8a and product geometry are represented in fig. 7b, 7c respectively.

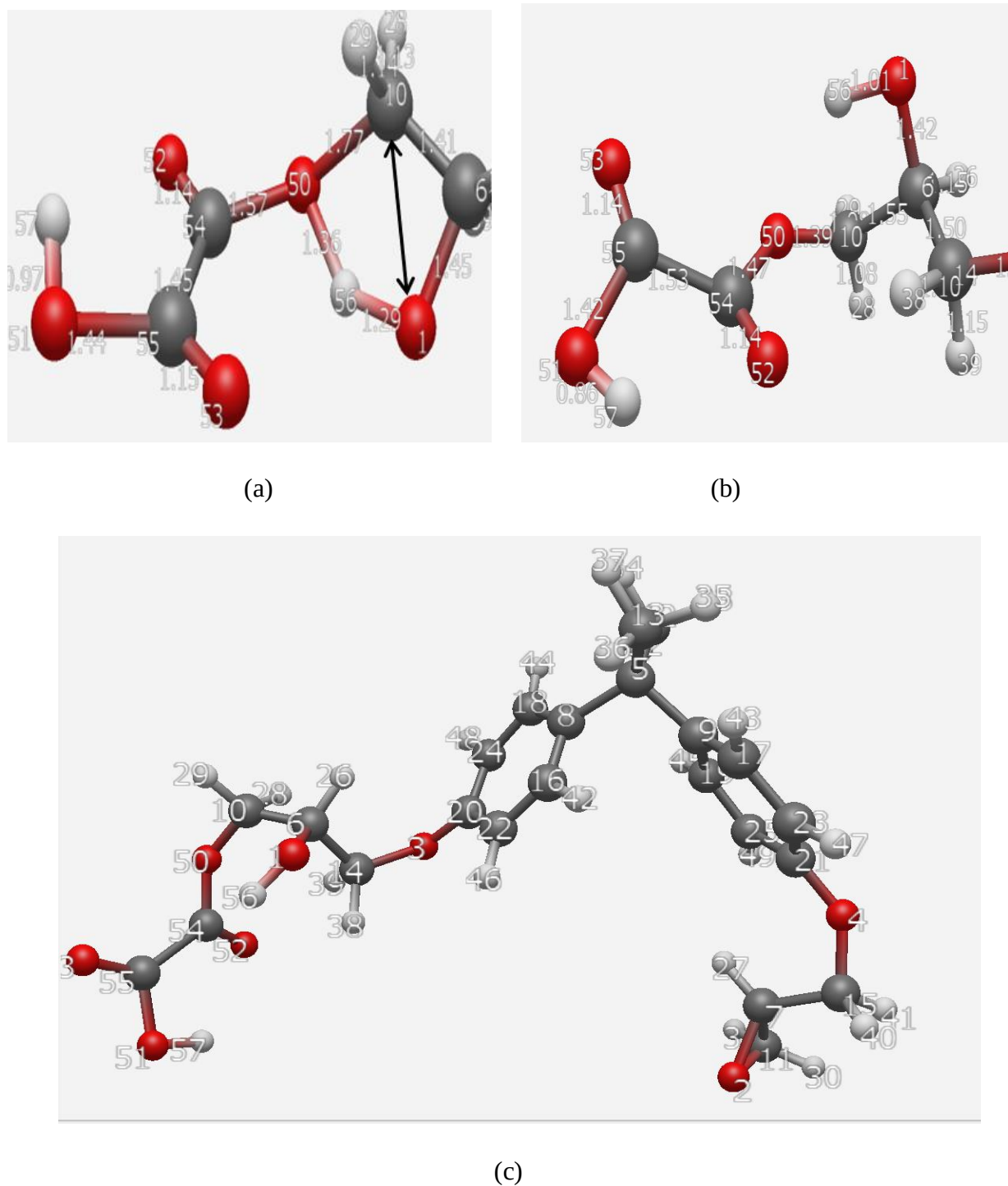


Figure 7: Snapshots from the biased MD trajectory: (a) transition state showing partial C-O bond formation and proton transfer, (b) product geometry immediately after transition state, and (c) final product geometry.

The transition state [Fig. 7a] shows partial elongation of the epoxide C–O bond (atoms 10 and 1) to 2.10 Å, as measured using the Avogadro measure tool, accompanied by simultaneous shortening of the forming C(epoxide)–O(acid) bond (atoms 50 and 10) to 1.77 Å. Figure 7a also captures the transfer of a proton (atom 56) from O(acid) to O(epoxide), supporting the observation that nucleophilic attack and ring opening occur in a stepwise, S_N2-like manner, consistent with ester formation in vitrimer systems. In the product geometry [Figs. 7b, 7c], the C–O (ester), C–O (β-hydroxy), and O–H (alcohol) bonds relax to approximately 1.31 Å, 1.42 Å, and 1.01 Å, respectively, which are in good agreement with experimental and DFT values reported for typical ester and alcohol linkages [28–31]. This validation confirms that COLVARS-based biasing reproduces the expected reaction pathway, and the resulting structures are suitable for subsequent polymerization studies and evaluation of thermomechanical properties.

3.2. Polymer growth and annealing

The evolution of root-mean-square-density (RMSD) value over two polymerization stages provides clear evidence of structural growth in the system [Fig 8a, 8b]. In stage 1 [Fig. 8a], which corresponds to polymerization between one DGEBA and one oxalic acid molecule, the RMSD value increases sharply at the beginning and quickly stabilizes near ~0.9 Å. This trend is consistent with small-molecule dimerization (localized bond rearrangement, then stable structure). However, in Stage 2 [Fig. 8b], where the Stage 1 dimer was duplicated and allowed to further react, the RMSD shows a more gradual increase and attains a higher equilibrium value near ~2.6 Å. This behavior indicates large-scale conformational changes arising from intermolecular linkages and increased conformational freedom within the growing polymer matrix, confirming progression of oligomerization. Overall, the RMSD trends are fully consistent with the expected transition from small-molecule dimerization to extended polymeric network formation.

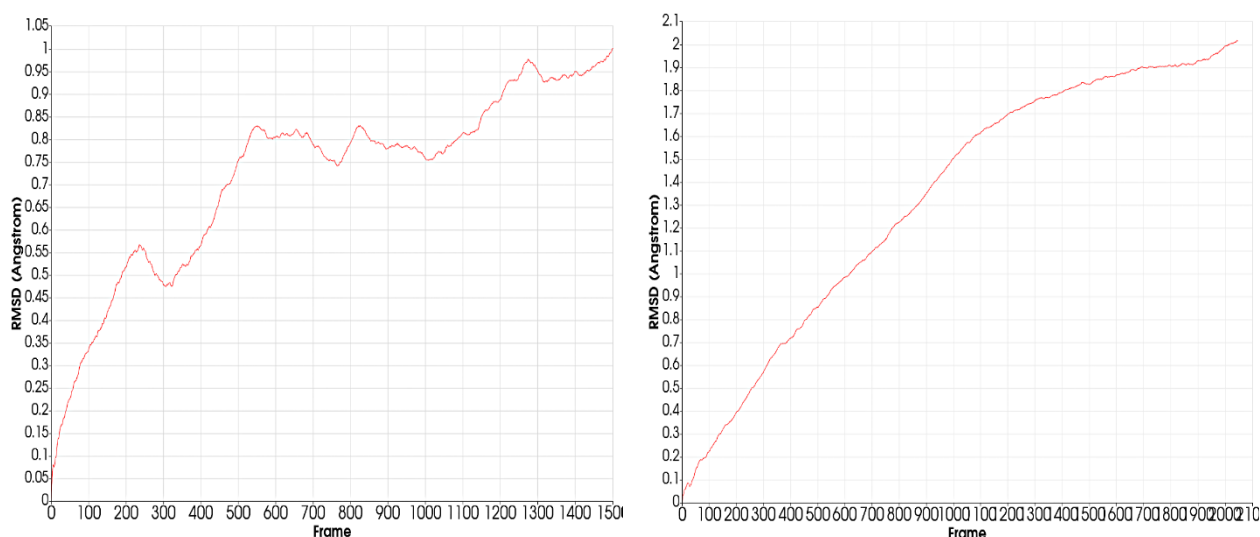


Figure 8: Root mean square deviation (RMSD) profiles for the DGEBA–oxalic acid polymerization. (a) Stage 1: reaction between one DGEBA and one oxalic acid molecule. (b) Stage 2: subsequent polymerization between two Stage 1 products. The RMSD evolution indicates structural relaxation and stabilization after each polymerization stage.

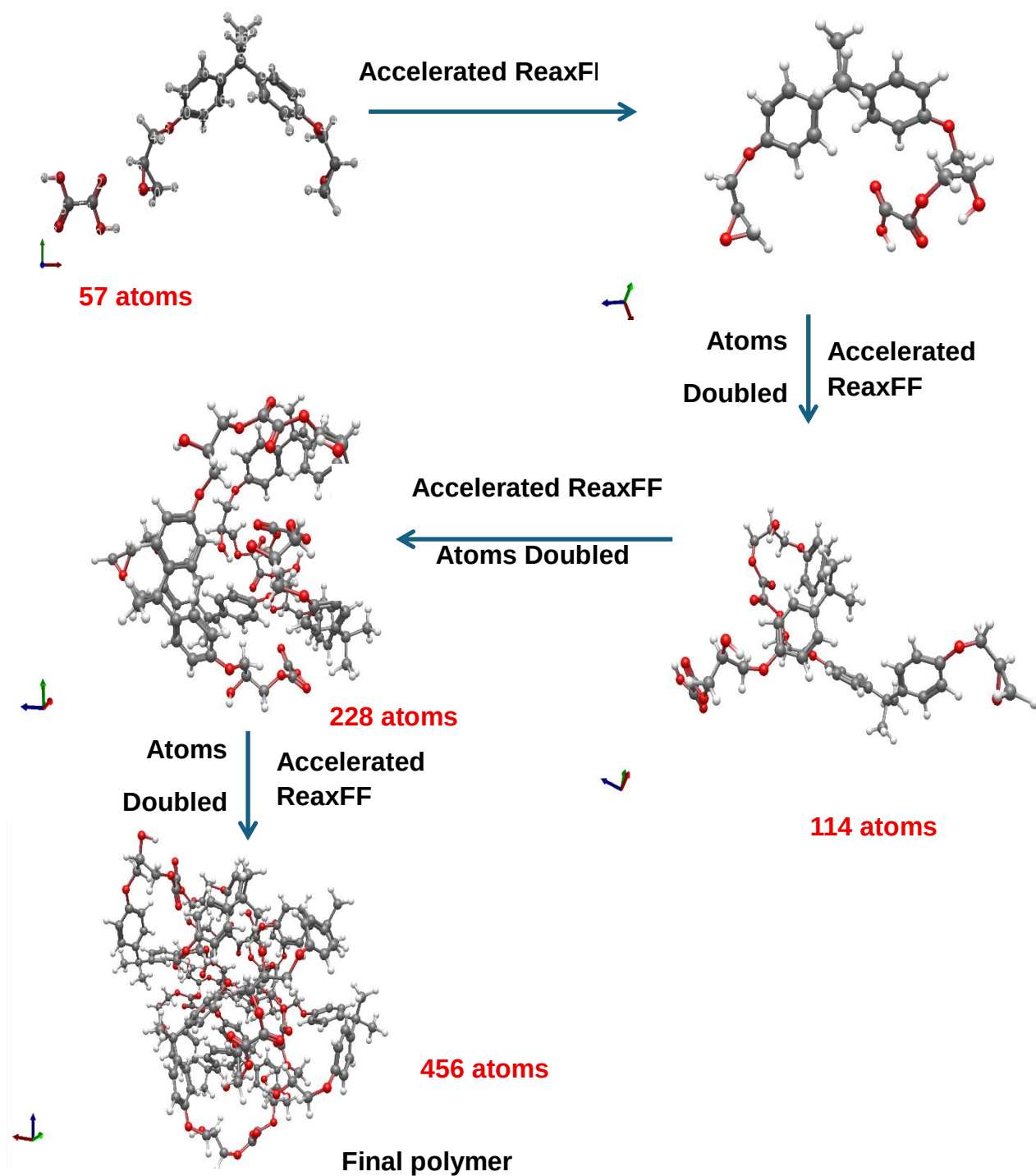


Figure 9: Polymerization scheme of DGEBA and oxalic acid. 1:1 stoichiometry of oxalic acid and DGEBA is maintained every steps

To approximate bulk behavior and capture interchain interactions, eight polymer chains of the final structure were placed in the simulation box for thermomechanical studies. The final

structure was annealed to remove the local heterogeneities. Two annealing cycles were performed to get the convergence in the density of polymer as shown in figure 10.

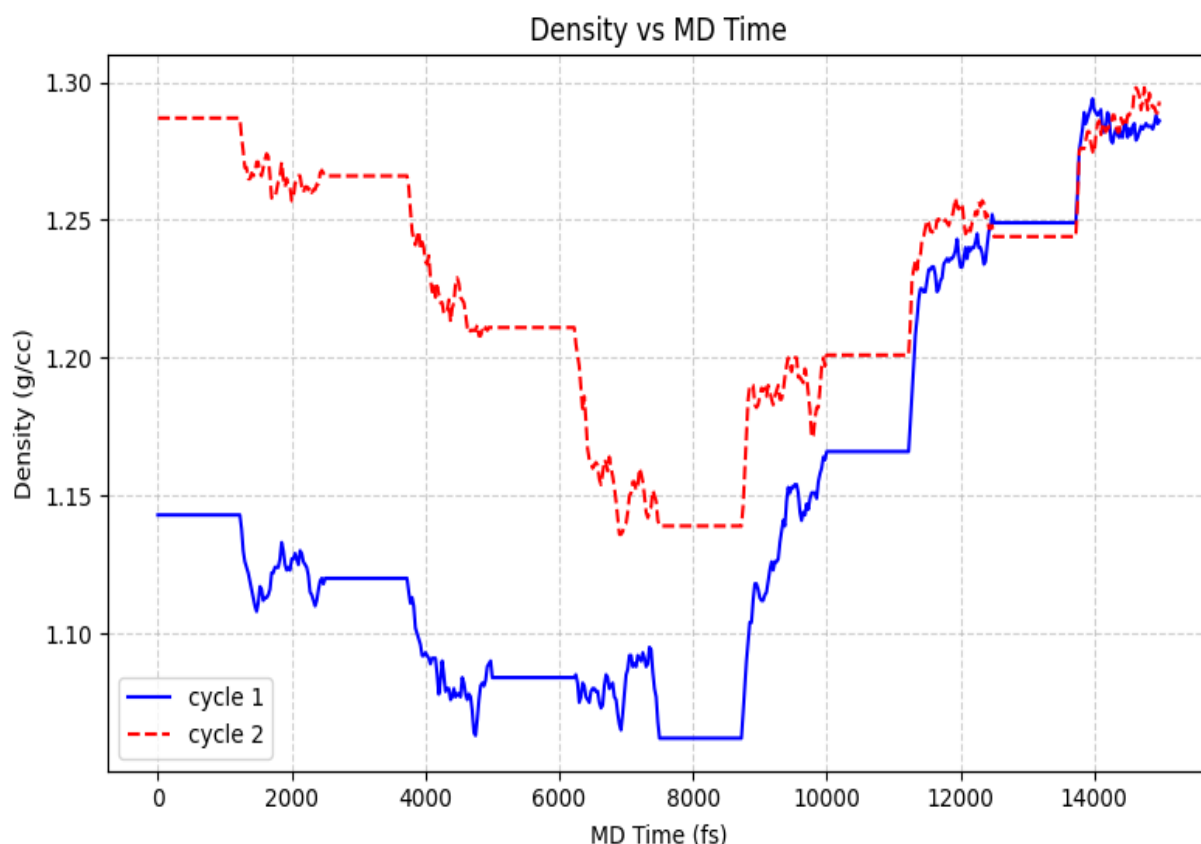


Figure 10: Evolution of density of polymer during two annealing cycles.

3.3. Thermomechanical Properties Analysis

The final structure after the second annealing cycle [Fig. 11] was used to study the thermomechanical properties of the DGEBA-oxalic acid vitrimer. At room temperature (300 K), the polymer density after annealing was $1.2975 \pm 0.0009 \text{ g}\cdot\text{cm}^{-3}$ [Fig. 12]. For comparison, Kamble et al.[32] reported a density of $1.215 \pm 0.006 \text{ g}\cdot\text{cm}^{-3}$ for the adipic-acid/DGEBA vitrimer build with similar strategy, while no literature results for the oxalic-acid/DGEBA polymer system are found since oxalic acid is not a commonly used curing agent. The higher density of the oxalic-acid network is expected due to its shorter crosslinker, which increases crosslink density, reduces free volume, and allows tighter molecular packing compared to the longer adipic-acid segments.

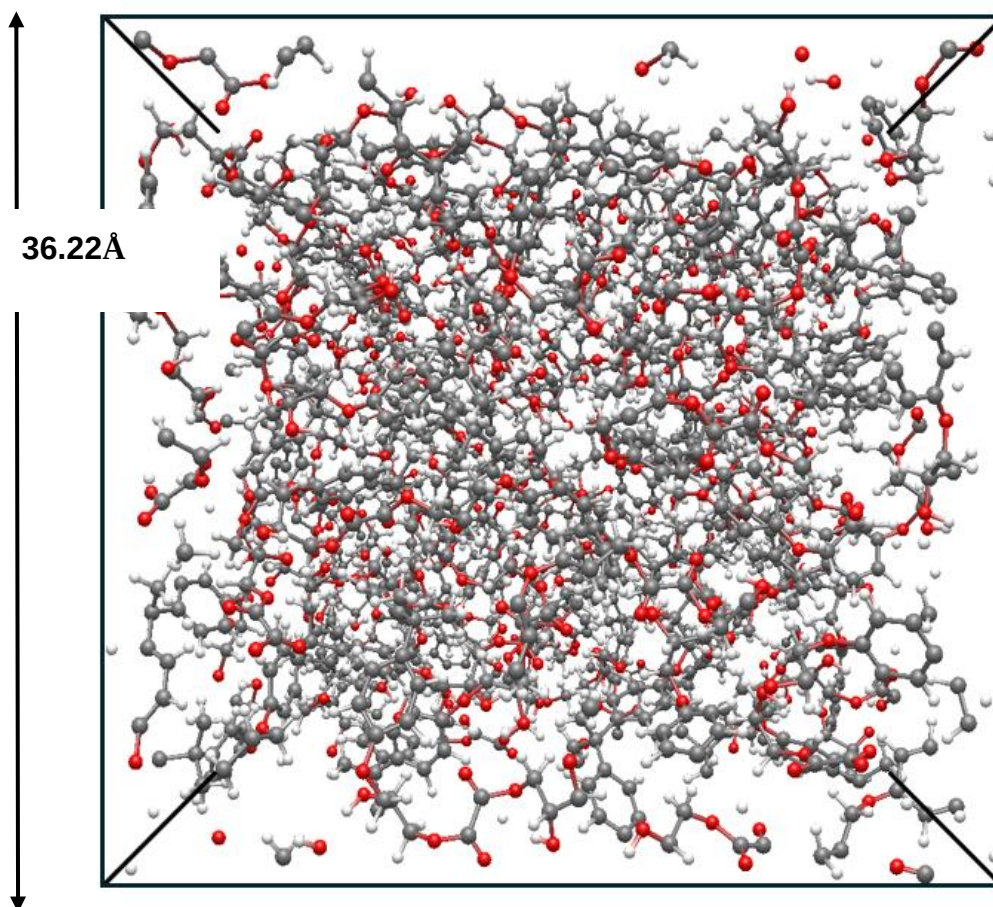


Figure 11: Annealed structure of DGEBA-Oxalic acid polymer used for thermo-mechanical properties investigation. Grey, red and white represent carbon, oxygen and hydrogen respectively.

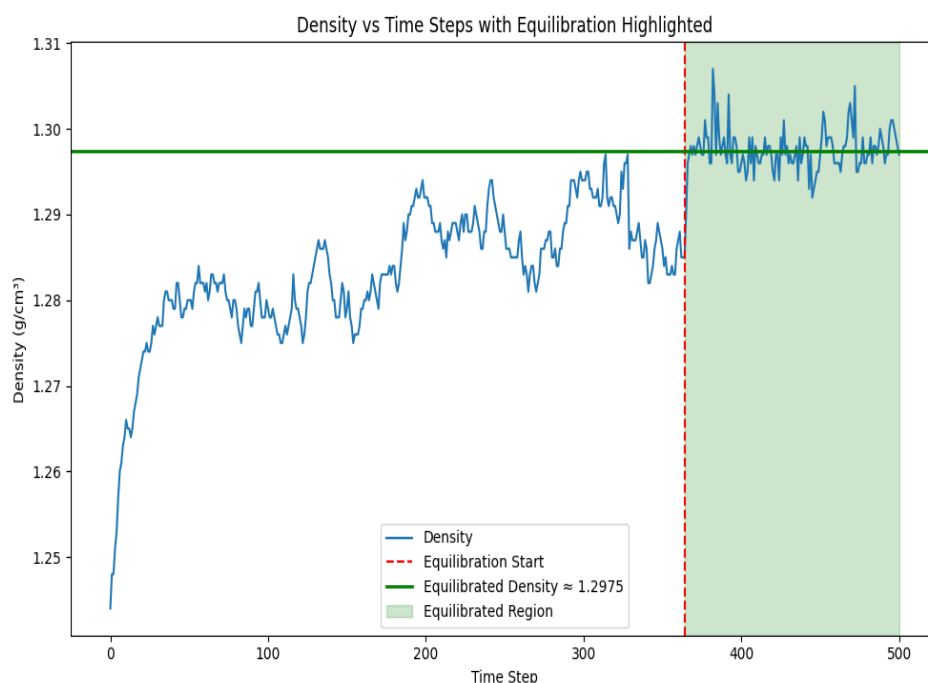


Figure 12: Density time-series data from final annealing segment at 300K. Shaded region represent the equilibration of density at 300K. The equilibrated density at 300K is reported as room-temperature density of DGEBA-Oxalic acid polymer.

Figure 13 presents the density–temperature relationship of the oxalic-acid–DGEBA polymer obtained from the simulated annealing MD simulations. A gradual decrease in density is observed at low temperatures, followed by a steeper decline at higher temperatures, indicating the transition from glassy behavior to rubbery behavior. The glass transition temperature was determined from the inflection point of temperature-density curve using cubic smoothing spline fitting [Fig. 14]. The second derivative of density with respect to temperature, $\rho''(T)$, crosses zero at 349.15(76°C), marking the concavity change of the curve and thus the T_g . Kamble et al. [32] reported a T_g of $\sim 42.8^\circ\text{C}$ for DGEBA cured with adipic acid. Compared to adipic acid, oxalic acid is a shorter and more rigid diacid, which leads to higher crosslink density and restricted chain mobility. Therefore, the simulated T_g of $\sim 76^\circ\text{C}$ for the DGEBA–oxalic acid system is consistent with this chemical trend and serves as a reasonable computational estimate in the absence of experimental data.”

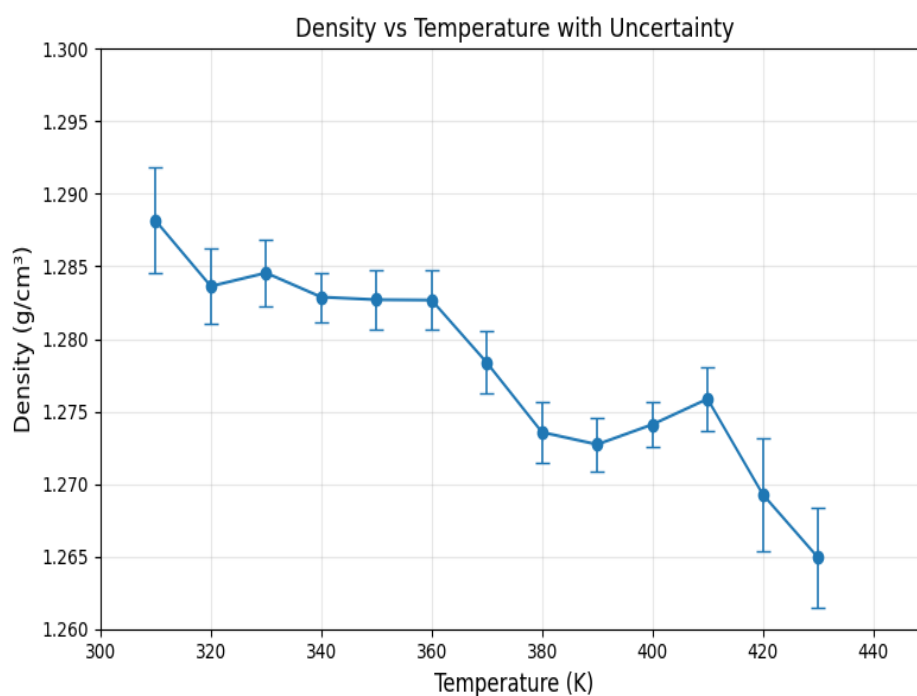


Figure 13: Temperature dependence of polymer density obtained from NPT molecular dynamics simulations. Symbols represent the average density at each temperature, while error bars indicate the standard deviation from independent sampling.

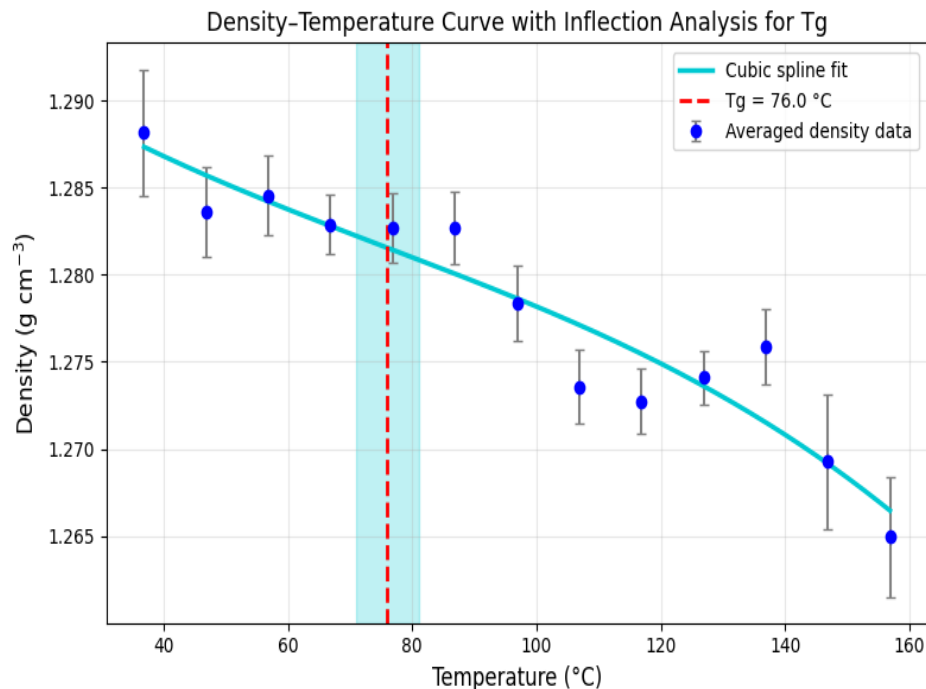


Figure 14: Determination of the glass transition temperature from the density–temperature curve using spline-based inflection point analysis. The red line indicates T_g (~76 °C), with the shaded region representing uncertainty in T_g

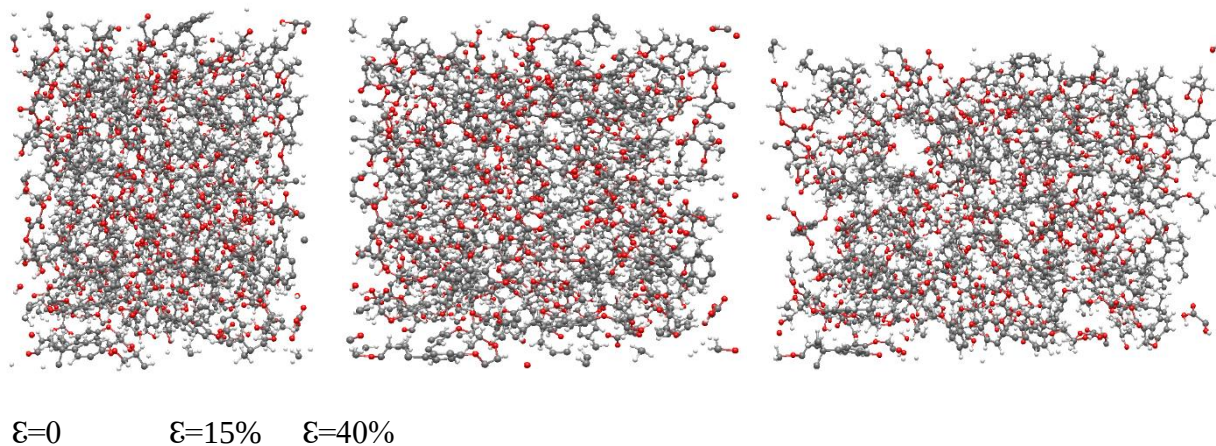


Figure 15: Evolution of deformation of DGEBA-oxalic acid polymer shown by snapshots at 0%, 15%, and 40% strain under a strain rate of 2×10^{-9} .

Figure 16a, 16b and 16c shows the stress-strain curve for annealed polymer strained along X, Y and Z direction respectively at $2 \times 10^9 \text{ s}^{-1}$ strain rate. A rolling average was used to smooth the scattered stress-strain data which are typical for MD simulations at finite temperature [33]. Yet, due to significant thermal vibrations of atoms at the atomistic scale, which are naturally captured in molecular dynamics simulations, small oscillations can be seen in the curve. Then, the Young's modulus was calculated from the stress–strain response in the 3–6% strain range, where

the response remained approximately linear for all three MD simulations. The predicted Young's Moduli value for vitrimer sample strained along X, Y and Z are shown in table 2.

Table 2: Comparison of Young Moduli results for different strain directions.

Strained Direction	Young Modulus
X	4.29
Y	2.67
Z	6.13

The simulated modulus (averaged in X, Y, Z directions) was found to be 4.36 ± 1.00 GPa for strain rate $2 \times 10^{-9} \text{ s}^{-1}$. The difference in modulus of polymer when strained at three different orthogonal directions can be explained by local structural heterogeneities and the specific spatial organization of molecules within the simulation box [23].

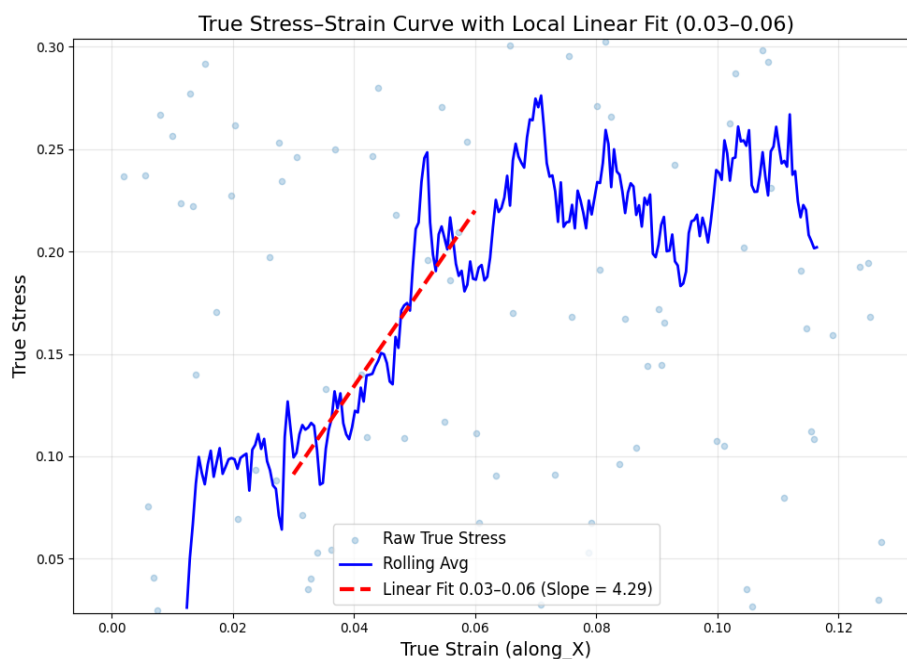


Figure 16: Stress–strain curves of the annealed DGEBA–oxalic acid polymer network at a strain rate of $2 \times 10^9 \text{ s}^{-1}$ along the X direction.

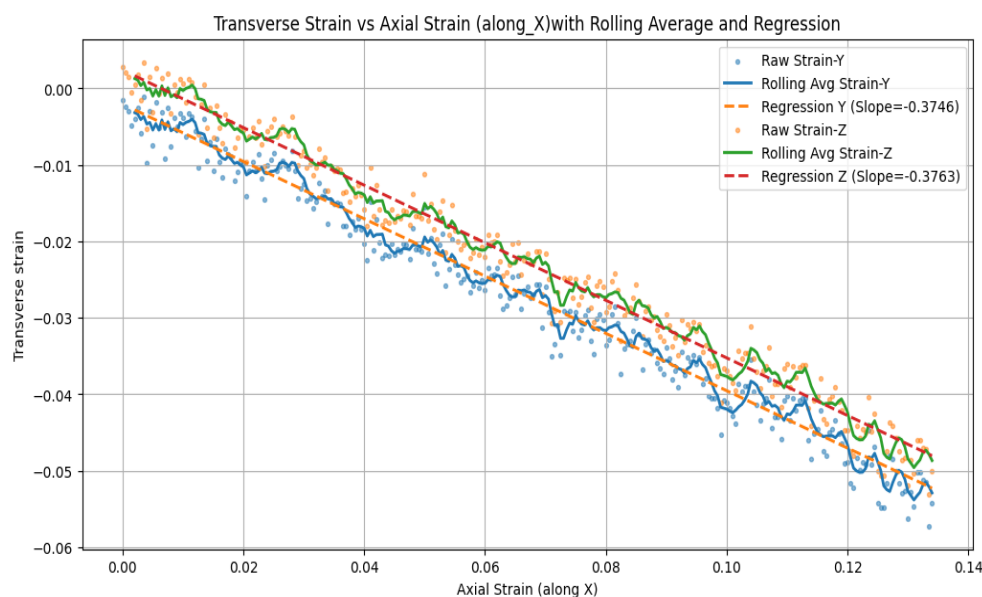


Figure 17: Transverse strain in Y and Z as a function of axial strain along X for the DGEBA–oxalic acid vitrimer composite under uniaxial tension, showing raw data, rolling-average smoothed curves, and linear regressions used to determine Poisson's ratio when strained along X.

Next, Poisson's ratio was determined from the transverse strain versus axial strain plots as shown in Figure 17. When the polymer was strained along one axis, the transverse strains in the two perpendicular directions were coupled, reflecting the simultaneous lateral contraction in perpendicular directions. Linear fits were applied to the data for both transverse directions, and the negative slopes of these lines were averaged to determine the Poisson's ratio. Table 3 presents the Poisson's ratios along the X, Y, and Z directions. The simulated value of poison ratio (averaged in X, Y, Z directions) was found to be 0.371 ± 0.012 .

Table 3: Comparison of Poison ratio results for different strain directions.

Strain directions	Poison's Ratio
Along X	0.37545
Along Y	0.38780
Along Z	0.34870

4. Conclusion

In this study, biased molecular dynamics simulations combined with reactive ReaxFF and COLVARS were used to model the epoxide-acid ring opening reaction in DGEBA-oxalic acid vitrimers. The simulation captured the stepwise S_N2 like mechanism where nucleophilic attack by the carboxylate oxygen opens the epoxide ring, followed by proton transfer to form the β-hydroxy ester linkage. This methodology produces the transition state and product geometries

consistent with DFT calculations and literature values, validating the accuracy of the approach. Hierarchical polymer growth and annealing revealed trends consistent with chemical intuition: shorter oxalic acid crosslinkers led to higher network density and elevated glass transition temperature, while stress-strain analysis showed anisotropic Young's modulus reflecting local structural heterogeneity.

Overall, this study highlights that COLVARS-based biased MD simulations can accurately reproduce the atomistic steps of vitrimer polymerization and provide a reproducible framework for developing vitrimer networks. This methodology can be extended to larger, more complex vitrimer systems offering a valuable computational platform for guiding the design of recyclable, self-healing, and mechanically robust polymer networks.

5. Supporting Information

COLVARS-based biasing strategy, Stress-strain Curves, Poisson ratio curves

6. Conflict of Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

7. Acknowledgement

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