

Reactive Machine Learning Force Field for Crosslinked Epoxy

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 Electronic Supplementary Information

Abstract Large-scale molecular dynamics (MD) simulations of crosslinked epoxy with quantum-level accuracy while capturing complex reactivity is a compelling yet unrealized challenge. In this work, through the construction of a chemical-environment-directing dataset, a reactive machine learning force field that accurately captures both reactive events and thermos-mechanical properties is developed. The force field achieves energy and force root-mean-square errors of 1.3 meV/atom and 159 meV/Å, respectively, and operates approximately 1200 times faster than ab initio molecular dynamics. MD simulations demonstrate excellent predictive capabilities across multiple critical thermos-mechanical properties (radial distribution function, density, and elastic modulus), with results being well consistent with experimental values. In particular, the force field can provide accurate prediction of the bond dissociation energies for typical bonds with a mean absolute error of 7.8 kcal/mol (<8%), which enables the simulation of tensile-induced failure caused by chemical bond breaking. Our work demonstrates the capability of the machine learning force field to handle the extraordinary complexity of crosslinked epoxy systems, providing a valuable blueprint for future development of more generalized reactive force fields applicable to most polymers.

Keywords Machine learning force field; Epoxy resin; Molecular dynamics; Bond breaking

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INTRODUCTION

Thermosetting resins are one of the most widely used lightweight materials that have significant applications in diverse fields, such as the aerospace industry and electronic packaging.^[1–4] In particular, the current interest in high-performance resins has been fueled by their tailorable properties, such as high-temperature resistance (>300 °C) and low dielectric constant, by controlling the monomers used and cross-linking microstructures within the resin.^[5–9] However, the critical challenge with respect to these resins is their unfavorable long-term durability under extreme environments caused by thermal or radiation aging, which usually involves complex microstructural evolution due to chemical bond breaking and reformation at the atomic level. Despite substantial experimental effort being devoted to providing valuable microstructural insights,^[10–12] the underlying mechanisms are still poorly understood because of the inability to visualize real-time atomic rearrangements and bond-breaking and reforming events.

Molecular dynamics (MD) simulations are powerful tools for capturing bottom-up characterization, which overcomes the

limitations of experimental approaches for studying atomic-scale phenomena.^[13–16] These computational methods offer unprecedented insights into the microstructural evolution and critical changes that occur during material degradation and failure. However, the effectiveness of MD simulations depends heavily on the accuracy of the interatomic potentials and the computational efficiency of the simulation algorithms.^[17–21] First-principles density functional theory (DFT) calculations, while providing precise modeling of the bond breaking and reformation processes, are constrained to relatively small system sizes and extremely short timescales (picoseconds), making them impractical for simulating complex polymer networks over long periods of time. Conversely, classical MD simulations typically rely on fixed-bond assumptions, which fundamentally prevent accurate representation of reactive events. Although reactive force fields such as ReaxFF^[21–26] have been developed to dynamically adjust the bond orders during simulations, their parameterization remains heavily dependent on manual tuning processes. This dependency significantly limits their adaptability to the complex and highly variable chemical environments of polymeric systems. Consequently, there is an urgent need to develop force fields that combine quantum mechanical accuracy with classical computational efficiency without being constrained by a preconceived notion of fixed chemical bonds or pre-existing knowledge of specific interactions.

Machine-learning-based force fields (MLFFs) are revolution-

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ary techniques that aim to narrow the gap between the accuracy of ab initio methods and the efficiency of classical force fields.^[27–44] Their unique advantage lies in their ability to autonomously capture intricate interatomic interactions and reactive processes without requiring preconceived notions of chemical bonding or prior knowledge of relevant interactions.^[41,45] This capability has enabled researchers to explore complex reactive events in various systems in unprecedented detail. For instance, Hedman *et al.* successfully simulated carbon nanotube growth processes using MLFFs^[32] while Zeng *et al.* identified nearly 800 previously unobserved chemical reactions in methane combustion studies.^[33] These achievements highlight the exceptional capability of MLFFs to capture reactive phenomena that traditional approaches cannot adequately represent. However, while significant progress has been made in developing MLFFs for inorganic materials and small molecular systems,^[33,36,46–47] their application to large-scale organic polymeric materials remains relatively underdeveloped. Current studies on small molecules relevant to combustion typically neglect intermolecular interactions and mechanical properties, focusing primarily on the molecular decomposition pathways.^[33,36,47] Additionally, polymeric systems present unique challenges owing to their nonergodic dynamics, which arise from chain entanglements, conformational heterogeneity, and nonperiodic structural arrangements.^[41,45] These complexities make the extension of MLFFs to polymeric materials particularly challenging.

In this study, we present highly reliable MLFFs for typical thermoset resins. The main goal of our work is to answer two fundamental questions: (1) whether MLFFs are suitable for modeling crosslinked polymer networks with intricate chemical environments and microscopic interactions and (2) whether MLFFs can accurately capture reactive behaviors that are crucial for understanding mechanical failure mechanisms. The MLFFs were trained on a comprehensive chemical-environment-directing dataset based on DFT calculations, and rigorously validated against key physical and mechanical benchmarks, including structural (radial distribution function (RDF)), thermodynamic (glass transition temperature, T_g), mechanical (Young's modulus), and chemical (bond dissociation energies, BDEs) properties. The validation results demonstrate that the MLFF can accurately capture these essential characteristics, establishing its robustness in simulating reactive polymer systems, including bond dissociation and mechanical failure.

METHODS

Dataset Construction

To create the MLFF dataset, various initial structures were first constructed, and then energy and force labels were obtained using ab initio molecular dynamics (AIMD) methods for subsequent model training. AIMD simulations were conducted using the CP2K software package.^[48,49] For each structure, AIMD simulations were conducted at multiple temperatures (300, 600, 1000, 2000, 3000, and 4000 K) to generate canonical ensemble (NVT) trajectories along with their corresponding precise energies and forces. In these calculations, core electrons were modeled using analytical Goedecker-Teter-Hutter (GTH) pseudopotentials.^[50] The selected exchange-correlation functional was

Perdew-Burke-Ernzerhof (PBE),^[51] augmented with D3 corrections^[52] to account for dispersion interactions. To ensure computational efficiency and accuracy, the energy cutoff values for the wavefunction and electron density were set to 60 Ry and 400 Ry, respectively. In this study, we employed a double- ζ Gaussian basis set with polarization functions (DZVP-MOLOPT).^[53]

Machine Learning Force Field

The MLFF was developed using the deep potential (DP) scheme derived from the DeePMD-kit package.^[54–55] In the DP scheme, atomic coordinates, forces (F), and energies (E) are extracted from quantum calculations to create the training set. The neural network model is built with atomic coordinates as the input and atomic energy and force as the output. The critical structure and parameters of the model were set as follows. The model included two networks: an embedding network and a fitting network. The size of the embedding network was set to (25, 50, 100) and the size of the embedding matrix was set to 16. The size of the fitted network was set to (240, 240, and 240). The cutoff radius was set to 6.5 Å and the descriptor decayed smoothly from 0.5 to 6.5 Å. The training process iteratively adjusts the model parameters to minimize the loss function (L), which measures the difference between neural network predictions and reference data. The loss function is defined as the sum of the squared differences in the predictions.

$$L = \frac{p_e}{N} \Delta E^2 + \frac{p_f}{3N} \sum_i |\Delta F_i|^2 \quad (1)$$

where the prefactors p_e and p_f are the weights of the total energy and atomic force, respectively. N represents the number of atoms in the structure. The prefactors p_e and p_f change dynamically during the optimization process as follows:

$$p(t) = p^{\text{limit}} \left[1 - \frac{r_1(t)}{r_1^0} \right] + p^{\text{start}} \left[\frac{r_1(t)}{r_1^0} \right] \quad (2)$$

where $r_1(t)$ and r_1^0 correspond to the learning rates at training step t and at the beginning, respectively. The prefactor varied from p^{start} in the first step and reached p^{limit} in the final learning step. This study uses p_e^{start} as 0.02, p_e^{limit} as 1, p_f^{start} as 1000, and p_f^{limit} as 1. The learning rate follows an exponentially decaying function

$$r_1(t) = r_1^0 \times d_r^{\frac{t}{d_s}} \quad (3)$$

where d_r and d_s denote the decay rate and steps, respectively. The initial and final learning rates were set to 1.0×10^{-3} and 3.0×10^{-8} , respectively. The model was trained for 1.0×10^6 iterations.

Molecular Dynamics Simulations

MD simulations were performed using a Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS)^[56] with an MLFF. In all calculations, periodic boundary conditions were implemented in all three directions of the simulation box, that is, the x -, y -, and z -directions. The Nosé–Hoover thermostat^[57] and barostat^[58–60] were adopted to control the temperature and pressure with temperature damping parameter T_{damp} (100 fs) and pressure damping parameter P_{damp} (1000 fs). A time step of 1 fs was used throughout all simulations, unless otherwise mentioned. The chemical structures of the molecules were visualized using OVITO.^[61]

In this study, we selected CVFF^[19] and ReaxFF^[21,26,62] as the nonreactive and reactive baselines, respectively. CVFF is one of the most widely used empirical force fields for polymer simulations and has demonstrated excellent agreement with experimental data across various systems such as EPON-862/DETDA,^[63] poly(methyl methacrylate) (PMMA),^[64] poly(dimethyl siloxane) (PDMS),^[65] and poly(lactic acid) (PLA).^[66] Furthermore, its parameter set is readily available in LAMMPS, which facilitates its reproducibility. ReaxFF, however, provides a precise description of bond breaking and formation through its bond order/bond distance relationship. However, ReaxFF simulations are approximately 10–20 times more computationally expensive per time step than CVFF simulations, constraining the system size and timescales that can be simulated. Therefore, we focused on the comparison of the behavior of tensile fracture and BDE prediction performance.

RESULTS

Model

A significant challenge in developing MLFFs is the construction of high-quality and diverse datasets for training. In this study, we focused on the E51/IPDA epoxy-amine system. Our primary dataset (Fig. 1) includes a wide variety of structures relevant to dynamic evolution, and comprises two key components. First, we constructed a diverse set of locally crosslinked monomer structures with IPDA:E51 coordination ratios ranging from 1:1 to 1:4 as well as representative bond-breaking configurations. To capture their thermodynamic behavior, we performed AIMD simulations and sampling across temperatures ranging from 300 K to 4000 K, as shown in Fig. 1(a). Each point in the figure represents a distinct structure positioned according to a principal component analysis of the learned descriptors for local atomic environments. Next, we investigated a polymer system consisting of 20 E51 monomers and 10 IPDA monomers with varying degrees of crosslinking and strain. As with the monomer-based dataset, we conducted AIMD simulations and sampling under diverse temperature conditions, as shown in Fig. 1(b). This study used approximately 1.6×10^5 DFT structure-energy-force data points covering 130 AIMD trajectories. The detailed parameters for the AIMD simulations can be found in the Section METHODS. The average runtime for each trajectory

on the AMD EPYC 7452 32-core machine was approximately 20 h.

It is worth emphasizing that this study incorporated a substantially larger number of high-temperature configurations ($T > 2000$ K) during dataset construction, offering two primary advantages. First, elevated temperatures accelerate the atomic-scale dynamics, enabling a more comprehensive exploration of the configuration space and alleviating the local sampling limitations inherent in low-temperature potential energy surface exploration. Second, high temperatures facilitate both bond breaking and formation, thereby allowing the training set to capture the critical features of reaction events. Consequently, this dataset design can significantly enhance the predictive accuracy and generalization capabilities of the trained force field in complex chemical environments.

Subsequently, a neural network-based MLFF was trained using these datasets, as outlined in the workflow diagram (Fig. 2a) and described in the Methods section. For detailed procedures on the model construction, please refer to references.^[54,55] Model training was completed on an NVIDIA A100-PCIE-40GB, with approximately 10 h required to train for one million steps. We then assessed its ability to predict the energies and forces on a subset of structures to validate the accuracy of the MLFF. For this test set, which was not used in the training process, the mean absolute error (MAE) and root mean square error (RMSE) of the energy and force predictions were computed. The regression plots in Figs. 2(c) and 2(d) demonstrate that the MLFF accurately reproduces DFT calculated energy and force values for the test dataset, achieving energy and force RMSE of 1.3 meV/atom and 159 meV/Å, respectively. These results are comparable to those reported for other MLFFs.^[32,33]

After training, the MLFF was employed in the MD simulations of E51/IPDA under diverse conditions. Its performance was systematically evaluated through a hierarchical validation framework, progressing from local structural descriptors to equilibrium thermodynamic properties, and ultimately to nonequilibrium mechanical responses and bond-breaking events. This multi-tiered validation approach enabled a comprehensive assessment of intra- and intermolecular interactions, providing critical insights into the macroscopic behavior of the polymer.

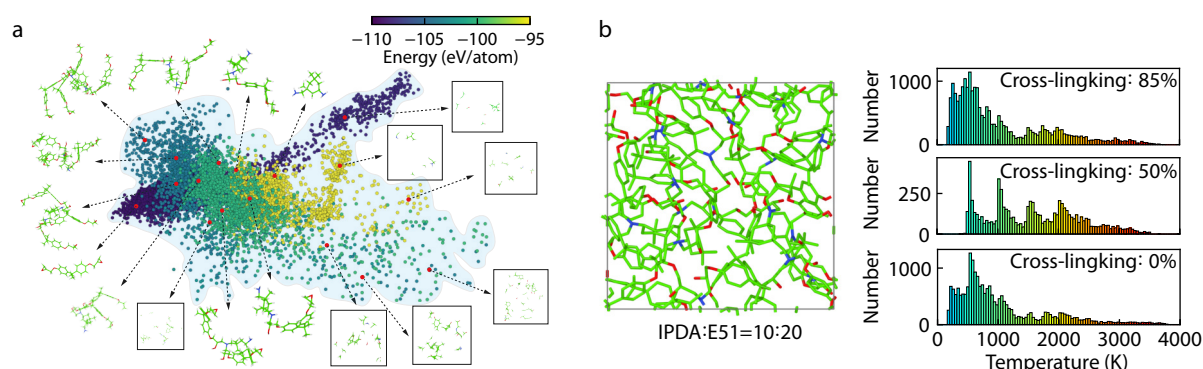


Fig. 1 The dataset used to train the MLFF. (a) The sketch-map where each colored dot represents an individual atomic configuration (structure). The position of each dot is determined by principal component analysis of the learned descriptors of the structures and its color indicates the corresponding energy of the structure. (b) The initial structure containing 20 E51 monomers and 10 IPDA monomers for performing AIMD simulations and the temperature distribution during the simulation process with different cross-linking degrees.

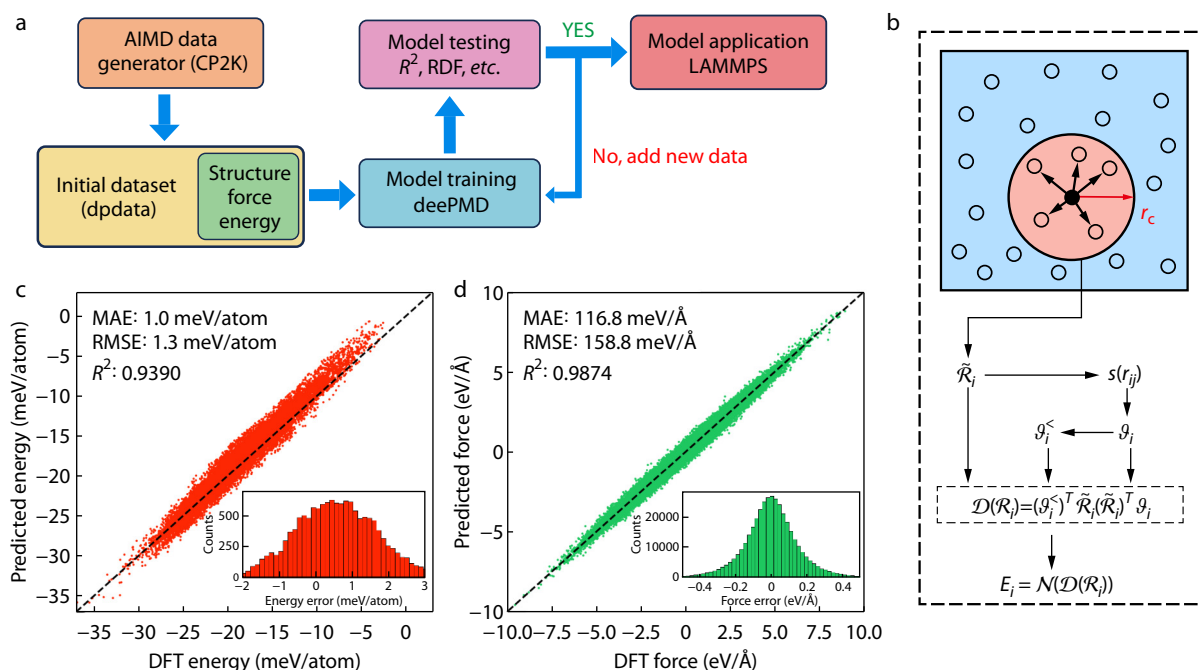


Fig. 2 A schematic of the machine learning framework and a comparison between DFT and MLFF predictions. (a) Training process of MLFF. (b) Mapping the local environment of a single atom to its atomic energy contribution. (c) Energy comparison between DFT and MLFF predictions, showing 14014 data points with evaluation using mean absolute error (MAE), root mean square error (RMSE), and R^2 . (d) Force comparison with 388,080 data points, evaluated similarly.

Radial Distribution Function

First, we evaluated the accuracy of MLFF in describing intramolecular interactions by comparing the RDFs obtained from the AIMD and MLFF simulations. The RDF, as a key structural descriptor, characterizes the distribution of interatomic distances and serves as a direct validation tool for force field accuracy. In this study, we focused on critical bond types, including C—C, C—N, C—O, C—H, N—H, and O—H.

The RDF was computed as an ensemble average over 200 MD frames at 300 K to ensure the statistical reliability. As shown in Fig. 3, the RDF curves from MLFF and AIMD exhibit strong agreement, which indicates that MLFF can accurately model the structure of polymers. Notably, AIMD requires approximately 20 h to simulate 2 ps, whereas MLFF completes the same simulation in just 54 s on an equivalent computational setup, operating roughly 1200 times faster than AIMD. This substantial speedup underscores the computational efficiency of the MLFF while maintaining high fidelity to the

AIMD structural predictions.

Interaction Energies and Density

Intermolecular interactions play a pivotal role in determining the macroscopic properties of polymers, including their mechanical strength and thermal stability. For example, strong intermolecular interactions enhance polymer rigidity and thermal stability, whereas weak interactions improve flexibility and processability. Consequently, an accurate description of intermolecular interactions is essential for evaluating the efficacy of MLFFs.

We compared the predicted intermolecular interaction energies of the MLFF with DFT reference calculations across various intermolecular distances to assess its predictive capability. As shown in Fig. 4, the MLFF successfully reproduces the characteristic distance-dependent trend: at short distances, the interaction energy decreases monotonically with increasing separation, whereas at longer distances, it gradually in-

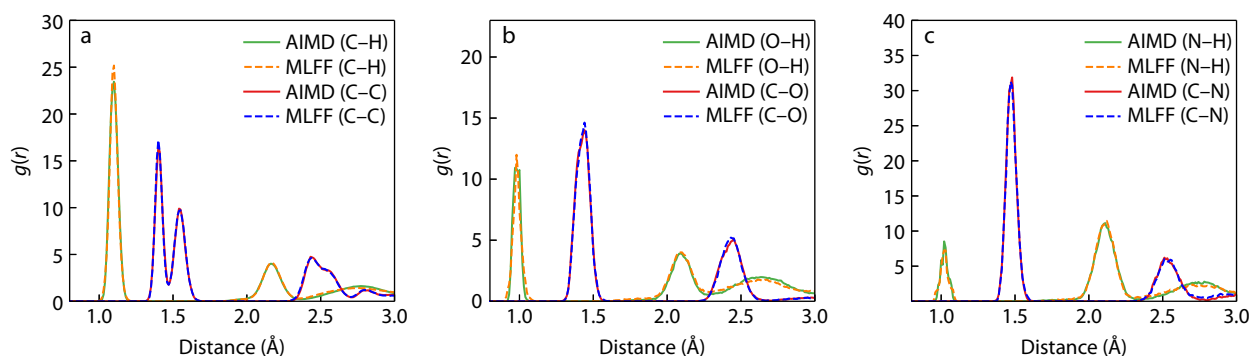


Fig. 3 Radial distribution function (RDF) obtained from AIMD and MLFF calculations: (a) C—C and C—H; (b) C—O and O—H; (c) C—N and N—H.

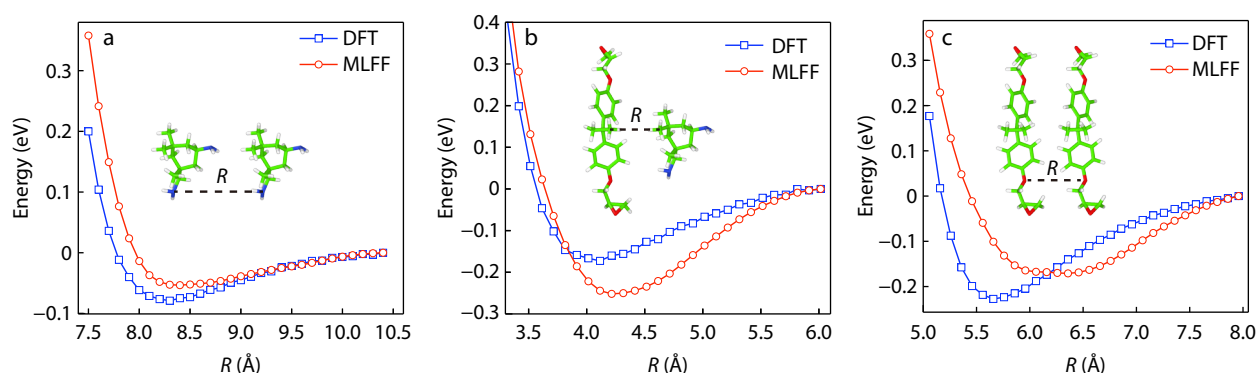


Fig. 4 Interaction energies for (a) IPDA-IPDA, (b) E51-IPDA, (c) E51-E51. Color code: green, C; blue, N; red, O; white, H.

creases. This behavior is consistent with the classical interaction potentials (e.g., the Lennard-Jones potential) and DFT results, confirming that the MLFF effectively captures the essential features of intermolecular interactions.

However, as illustrated in Fig. 4, the MLFF predictions were more accurate for smaller molecules (e.g., IPDA-IPDA) than for larger molecules (e.g., E51-E51). This size-dependent discrepancy primarily stems from the cutoff radius limitation ($r_c = 6.5$ Å in this study), which defines the spatial range within which atomic interactions are explicitly modeled by the neural network. Interactions beyond this cutoff were not considered, resulting in discrepancies in the interaction energies compared with the DFT calculations. Therefore, incorporating long-range interactions beyond the cutoff remains a key challenge for the current MLFF frameworks.

Subsequently, MLFF-based MD simulations were performed to compute the densities of various mixed components. As shown in Fig. 5(a), the MLFF effectively distinguished systems with different mixing ratios: pure E51 exhibited the highest density, pure IPDA the lowest, and the density progressively increased with the E51 fraction. These trends agree with those obtained from CVFF-based MD simulations, as illustrated in Fig. 5(b).

However, the MLFF systematically overestimated the polymer density relative to that of the CVFF. This discrepancy can be attributed to two primary factors. First, the MLFF was trained on data from higher-fidelity DFT calculations, and differences in the underlying methodologies naturally led to discrepancies between the MLFF and CVFF results. Second, the limited cutoff radius in the MLFF restricts the accurate modeling of long-range interactions, which subsequently affects density predictions. We also trained MLFFs using cutoff radii ranging from 5.5 Å to 6.5 Å and compared their performance in terms of R^2 and RMSE (Fig. S2 in the electronic supporting information, ESI). The results show that, while increasing the cutoff slightly reduces the model accuracy, the change is minimal. This occurs because a larger cutoff increases the complexity of the atomic local environment, requiring more training data and steps to fit the expanded configurational space. In addition, we performed MD simulations using MLFFs trained with different cutoff values and obtained the time evolution of density at 300 K. The simulation results show that the predicted density varies with the choice of cutoff, as shown in Figs. 5(c) and 5(d). For reference, the experimental density of pure E51 ranges from approximately 1.16 g/cm³ to

1.22 g/cm³,^[67–69] and that of pure IPDA was approximately 0.92 g/cm³.^[67] When compared to the 5.5 Å cutoff, the MLFF with a 6.5 Å cutoff gives predictions much closer to the midrange value of E51 (1.19 g/cm³) and also closer to the density of IPDA (0.92 g/cm³). Compared with the CVFF results, the MLFF performs better for E51, whereas it is slightly less accurate for IPDA. However, as the cutoff radius increased, the experimental density value tended to approach. We also compared the densities obtained using the ReaxFF. The results indicate that ReaxFF-2011^[62] predicts the density of E51 to be approximately 1.20 g/cm³ and the density of IPDA to be around 1.07 g/cm³, while ReaxFF-2018^[26] predicts the density of E51 to be approximately 1.23 g/cm³ and the density of IPDA to be around 0.91 g/cm³. These results suggest that, in addition to the significantly overestimated density of IPDA predicted by ReaxFF-2011, the remaining density deviations were within 10% of the experimental values. This demonstrates that our MLFF is on par with traditional force fields, such as CVFF and ReaxFF, in terms of predicting the polymer densities.

In addition, we compared the efficiencies of different cutoff radii (Table S2 in ESI). When the cutoff radius increased from 5.5 Å to 6.5 Å, the training time for one million steps increased by approximately 1.29 h, and the MD simulation efficiency decreased by about 18.02%. In this study, considering the trade-off between accuracy and efficiency, and following previous literature,^[70,71] we selected a cutoff radius of 6.5 Å for the study. Addressing these long-range interactions remains a critical direction for improving the accuracy of the MLFF in polymer simulations.

Moreover, we compared the computational efficiency of different types of force fields on the same machine (Table S3 in ESI). The results indicate that the simulation efficiency of the CVFF is approximately 30 times that of the ReaxFF and approximately 90 times that of the MLFF. This highlights the fact that the current MLFF still has a relatively low computational efficiency.

Glass Transition Temperature

T_g is crucial for determining the mechanical behavior of polymers. It marks the transition from a glassy, brittle state to a rubbery, flexible state, serving as a critical indicator of the thermal stability, elasticity, and overall performance.^[72,73] Despite its importance, accurately predicting T_g remains challenging owing to the complex interplay of factors, such as polymer chain rigidity,

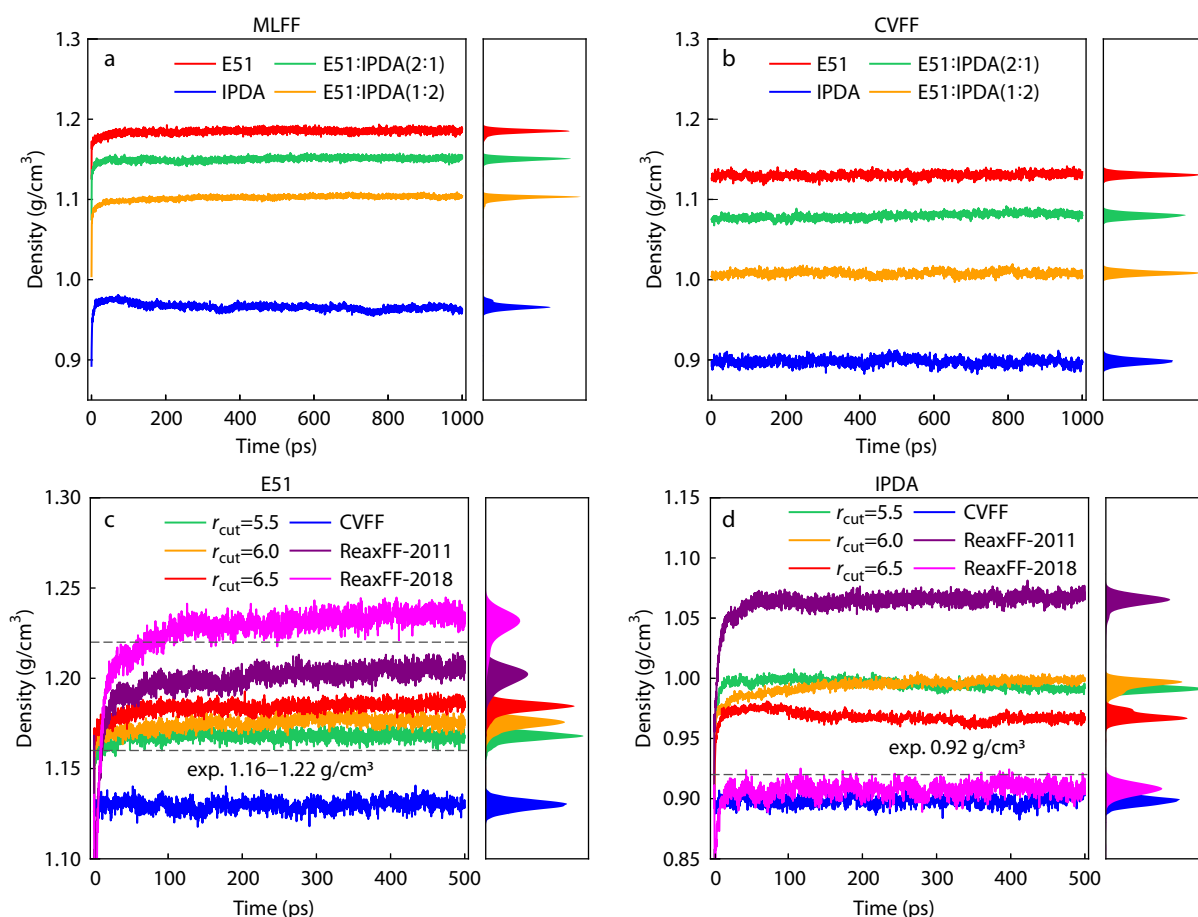


Fig. 5 Density of systems. (a) The density variation of the system with different mixing ratios was simulated for 1 ns using MLFF at 300 K. (b) The density variation of the system with different mixing ratios was simulated for 1 ns using CVFF at 300 K. (c) The density of E1 with different force fields was simulated for 500 ps at 300 K. (d) The density of IPDA with different force fields was simulated for 500 ps at 300 K.

entropic contributions, and intermolecular forces. Traditional models often fail to capture these interdependencies, as they typically rely on simplified representations of molecular interactions that do not fully reflect polymer behavior.^[8,74] Therefore, we further investigated the temperature-dependent response of the density predicted by MLFF to assess its predictive capability for T_g .

This study calculated the T_g of the E1/IPDA system using MLFF and compared the results with those obtained using the classical CVFF. A simulation box was constructed containing 256 E1 monomers and 128 IPDA monomers with initial dimensions of 56 Å × 56 Å × 56 Å. Because of the current limitations of MLFF in simulating crosslinking reactions, the crosslinked polymer sample in this work was generated using a dynamic crosslinking script written by DeJoannis, achieving a final crosslinking degree of 92% (Fig. S1 in ESI for details). The CVFF was utilized for the initial equilibration because of its computational efficiency and compatibility with complex polymer systems. Specifically, the structure was equilibrated in an isothermal-isobaric (NPT) ensemble at 650 K and 0.1 MPa for 5 ns to obtain a well-relaxed initial configuration. Subsequently, MD simulations were performed using the MLFF. The CVFF-equilibrated structure underwent energy minimization, followed by further equilibration in the NPT en-

semble at 650 K and 0.1 MPa for 800 ps to eliminate stress and stabilize the structure at high temperatures. Finally, the system was simulated using MLFF under a constant pressure (0.1 MPa) with cooling rates of 0.2 and 1 K/ps. T_g was identified as the inflection point on the specific volume-temperature curve, which was determined by piecewise linear fitting of data from two distinct temperature ranges: 150–350 K (glassy region) and 450–650 K (rubbery region).

As shown in Fig. 6, the MLFF predicted a T_g of 408 K at a cooling rate of 0.2 K/ps, which is in close agreement with the experimental value of 436 K^[75] and surpasses the CVFF prediction of 398 K. At a cooling rate of 1 K/ps, the MLFF further demonstrated its robustness by yielding a T_g of 436 K compared with the CVFF prediction of 447 K. These findings underscore the reliability of MLFF in capturing the thermal properties of crosslinked polymers under varying cooling conditions with improved alignment to the experimental data.

The superior performance of the MLFF in predicting T_g was attributed to its capacity to accurately model the complex intermolecular interactions within the crosslinked epoxy network. Unlike classical force fields that oversimplify these interactions, the MLFF employs a high-fidelity training dataset along with an efficient machine learning framework. These features allow the model to extend the temporal and spatial

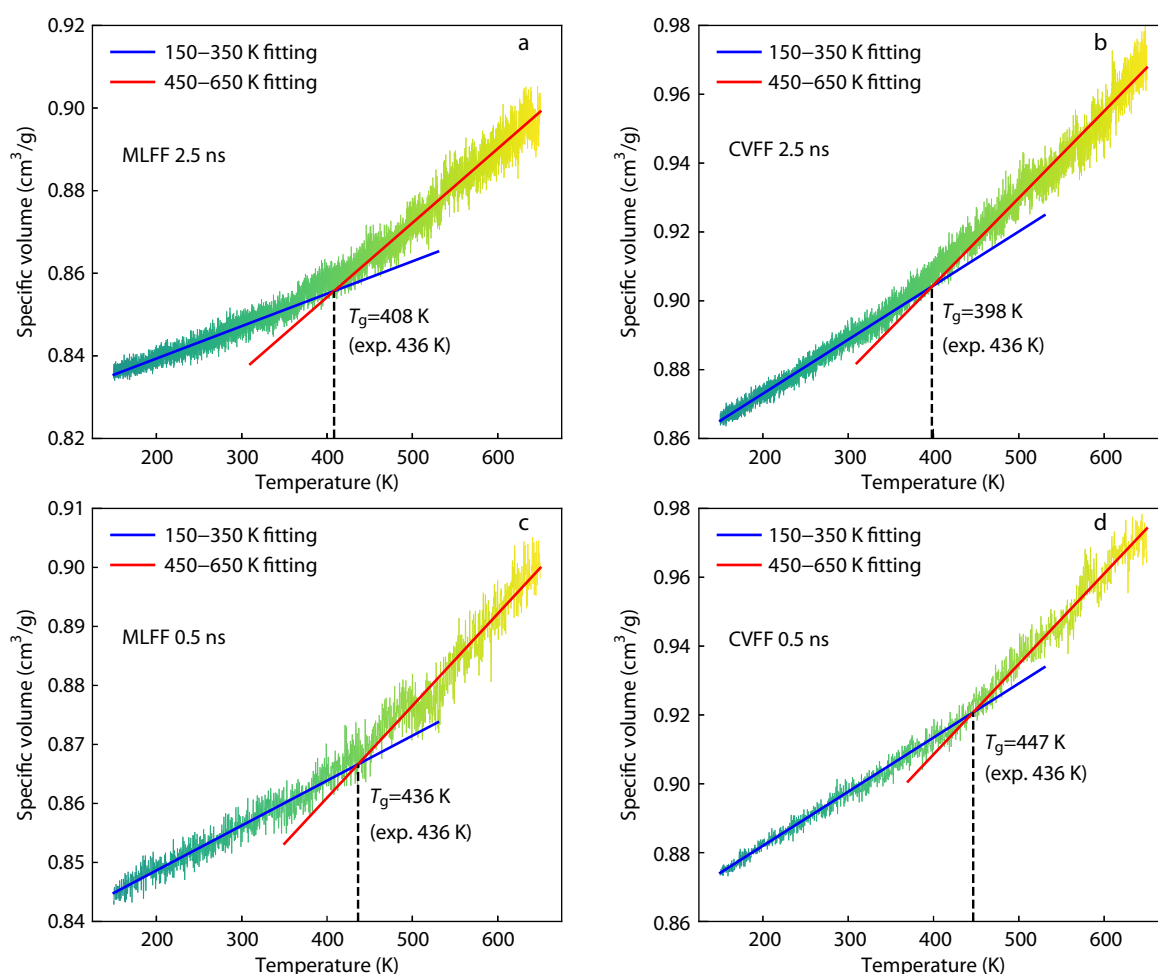


Fig. 6 Simulated specific volume-temperature curves for E51/IPDA system. (a) MLFF result with a cooling duration of 2.5 ns. (b) CVFF result with a cooling duration of 2.5 ns. (c) MLFF result with a 0.5 ns cooling duration. (d) CVFF result with a 0.5 ns cooling duration. T_g is determined by fitting specific volume-temperature curves between 150–350 K (blue line) and 450–650 K (red line).

scales of the simulations without sacrificing precision, making it particularly effective for studying the dynamic evolution of polymer systems.

Mechanical Properties

To validate the accuracy of the MLFF in predicting the mechanical properties of E51/IPDA, we compared the atomic forces calculated by DFT with those predicted by the MLFF under varying tensile conditions. DFT provides highly accurate atomic force data, whereas MLFF enables large-scale simulations of epoxy resins. This section aims to demonstrate the performance of MLFF in force prediction, particularly under various tensile conditions, to further assess its practical applicability.

First, we simulated the tensile deformation of the E51 monomer using MLFF and extracted the structures at various tensile strains. We then compared the forces on each atom calculated by DFT with those predicted by MLFF, as illustrated in Fig. 7. The results indicate that within the tensile range of 0%–19%, the MLFF closely reproduced the DFT force data, with differences within acceptable error margins. Even at higher strains (e.g., 10%–19%), the MLFF maintained good agreement with the DFT results. The prediction accuracy of MLFF remained high across the entire strain range, with R^2

values consistently exceeding 90%. The analysis further revealed that the MLFF exhibited a higher prediction accuracy in the lower strain range (0% to 13%), while errors increased slightly at strains above 13%. We attribute this phenomenon to the sparser training data available at higher strains. To enhance the prediction accuracy for larger strains, future research should expand the training set to encompass a broader strain range. Despite some discrepancies, the MLFF demonstrates a high degree of correspondence with the DFT results and significant advantages in terms of computational efficiency. With further expansion and optimization of the training dataset, MLFF is expected to play an increasingly important role in materials science simulations.

Next, simulations were conducted at 300 K with a cross-linking degree of 92% to assess the predictive capabilities of the MLFF regarding the stress-strain responses, Young's modulus, and Poisson's ratio. The simulation results are shown in Fig. 8. The stress-strain curve derived from the MLFF exhibits a distinct stress drop beyond a critical strain of approximately 72% (Fig. 8a), which is indicative of bond breakage and structural failure. In contrast, the CVFF simulation did not capture this behavior because its stress-strain curve lacked a significant stress drop. Fig. 8(b) displays the local microstructure at

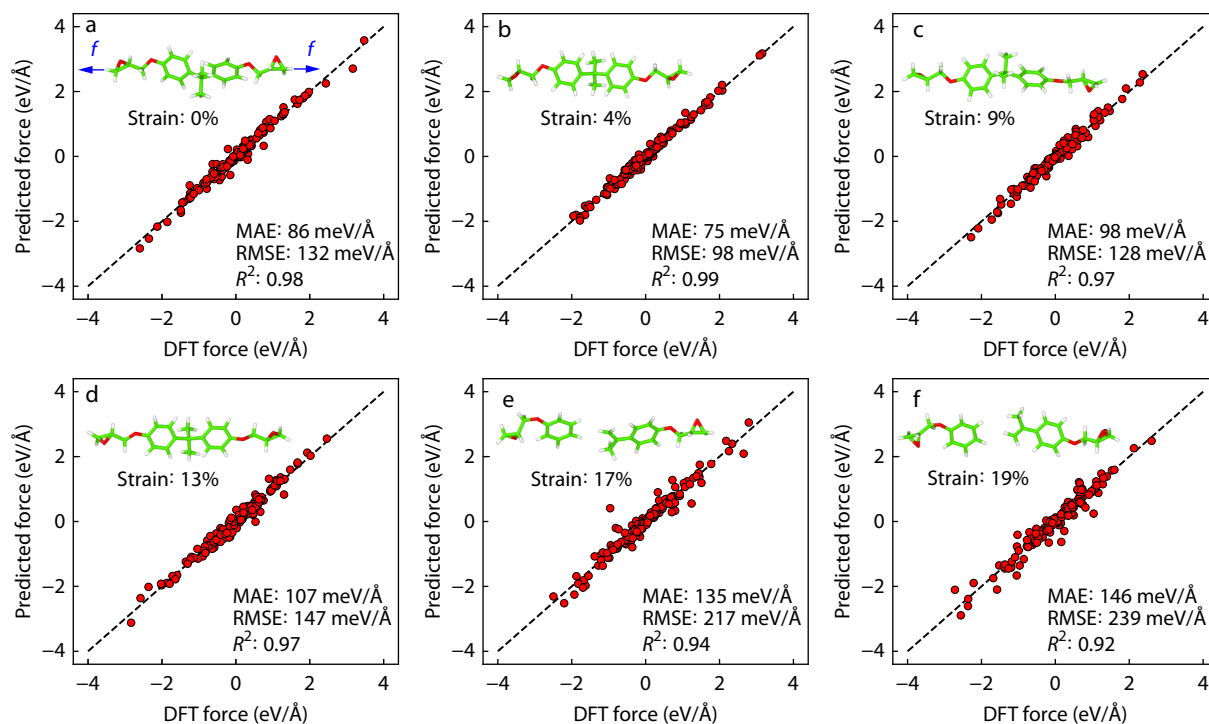


Fig. 7 The comparison of forces on each atom between DFT and MLFF predictions under different tensile strains: (a) 0%, (b) 4%, (c) 9%, (d) 13%, (e) 17%, (f) 19%.

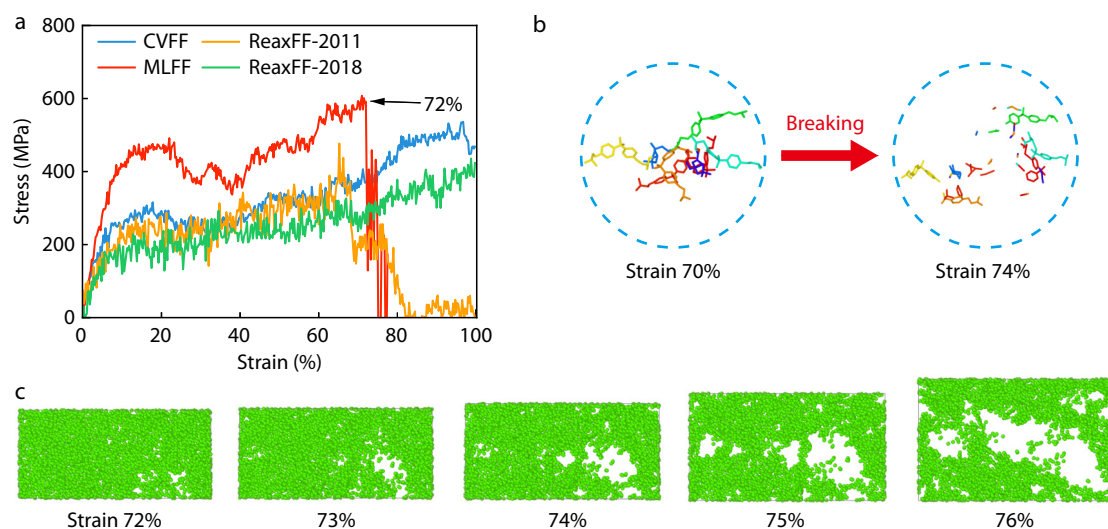


Fig. 8 Stress-strain behavior under uniaxial deformation. (a) Stress-strain curves; (b) Localized molecular structures at 70% and 74% tensile strains simulated by MLFF; (c) Structural evolution under varying tensile strains simulated by MLFF.

70% and 74% strain, as simulated by MLFF, with identical colors representing identical molecules. This figure demonstrates that multiple molecules fracture under a large strain, thereby validating the MLFF's predictive capability for the stretching behavior.

Furthermore, atomic-level simulations enable the real-time observation of structural evolution during fracture. To better visualize the local features and details, we extracted a 20 Å thick slice along the y-axis from the complete simulated structure, as shown in Fig. 8(c). This slice illustrates the evolution of the failure process as simulated by the MLFF, which is critical

for understanding the onset of mechanical failure and overall durability of the epoxy resin under extreme loading conditions.

Although the MLFF model can capture the fracture behavior, we realized that the predicted fracture strain (>70%) was significantly higher than the typical experimental value for epoxy resins (<15%). Therefore, we conducted an in-depth study of this phenomenon. Fracture in the experiment occurred because the prepared material may contain small cracks, bubbles, or impurities. These defects become points of stress concentration, leading to the propagation of fracture

lines during the tensile process, eventually causing fracture to occur. Because the initial structure in this study was defect-free, it was expected that the fracture strain would be higher than the typical fracture strain of industrial epoxy resins under experimental conditions. To verify this, we included the stretching simulation results of the same system using the ReaxFF-2011^[62] and ReaxFF-2018^[26] force fields, as shown in Fig. 8(a). The results show that the fracture strain remained above 70%, which is consistent with the predictions of the MLFF. This suggests that the high fracture strain is not due to the 'over-softening' of a single force field or random errors, but rather reflects the inherent extensibility of the idealized network. In addition, an excessively high fracture strain is a common issue in MD simulations, as demonstrated by Yu *et al.* for DGEBA + MDA^[76] and Miura *et al.* for DGEBA+44DDS^[77], both of which reported fracture strains exceeding 100%.

Quantitative analysis of the stress-strain data within the 0–2% strain range provided further insight into the predictive differences between different force fields. As shown in Fig. 9(a), the Young's modulus predicted by the MLFF (6.4 GPa) is higher than those predicted by the CVFF (4.1 GPa), ReaxFF-2011 (2.5 GPa), and ReaxFF-2018 (2.5 GPa). The experimentally measured modulus for E51/IPDA ranges from 2.65 GPa to 4.85 GPa.^[75,78–80] The overestimation of Young's modulus involves two primary aspects: firstly, MLFF tends to overestimate Young's modulus relative to CVFF and ReaxFF, and secondly, MLFF's predictions exceed the experimental values.

The MLFF is a model that learns force field parameters from large datasets derived from first-principles calculations. Consequently, it tends to provide predictions that align well with the DFT results. In contrast, CVFF and ReaxFF are classical force-field models based on predefined parameters, which are primarily derived from experimental and empirical data. Consequently, these methods differ in their data-fitting approaches, leading to observable discrepancies in their predictions. To verify the differences between the CVFF, ReaxFF, MLFF, and DFT, we predicted the atomic forces for the same structure using DFT, MLFF, CVFF, and ReaxFF (Fig. S3 in ESI). It can be seen that the results of MLFF align well with those of DFT, whereas CVFF and ReaxFF perform less accurately. This divergence likely contributes to the observed overestimation of Young's modulus when using MLFF as compared to CVFF

and ReaxFF.

The overestimation of Young's modulus by MLFF relative to the experimental values may arise from two key factors. First, experimental materials often contain microscopic defects, which can reduce the actual Young's modulus compared with the theoretical value predicted by computational models. Second, this study employed a higher strain rate ($5 \times 10^7 \text{ s}^{-1}$), whereas experiments were typically conducted at strain rates between 10^{-3} s^{-1} and 10^{-1} s^{-1} . The rate effect causes the material to exhibit increased stiffness under high-speed loading, resulting in discrepancies between computational predictions and experimental observations.

Furthermore, although the MLFF results generally align well with the DFT predictions, the differences between the DFT and experimental data are more nuanced. Large-scale DFT MD simulations are computationally expensive and often impractical, which limits our ability to conduct comprehensive simulations. As a result, the MLFF was validated by comparing key indicators such as energy, force, and RDF. A deeper investigation into the discrepancies between DFT and experimental results would require the consideration of factors such as pseudopotential selection and van der Waals interactions. Because datasets obtained with different pseudopotentials or van der Waals interactions cannot be combined, exploring these variables would require significant computational resources, making such research difficult to pursue at present. In conclusion, the overestimation of the Young's modulus by MLFF arises from multiple factors, including differences in strain rates and material imperfections. To refine the simulation accuracy and achieve results closer to the experimental values, further in-depth research is necessary to optimize computational models and methodologies.

In addition, as shown in Fig. 9(b), Poisson's ratio was also calculated from the strain-stress data, with values of 0.36, 0.34, 0.45, and 0.41 for MLFF, CVFF, ReaxFF-2011, and ReaxFF-2018 respectively. The predicted results of MLFF and CVFF fall within the typical range for cross-linked polymers (0.33–0.38),^[78,81,82] while the results predicted by ReaxFF are somewhat higher, further validating the accuracy of MLFF in predicting the fundamental mechanical properties.

In short, MLFF can effectively reproduce the fracture behavior, whereas CVFF struggles to capture these phenomena,

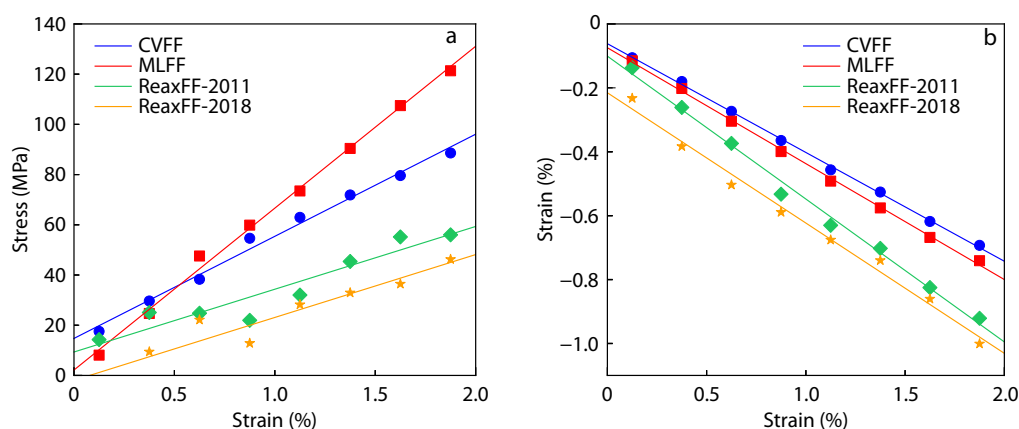


Fig. 9 Young's modulus and Poisson's ratio calculated from strain responses to uniaxial tensile strain. (a) Young's modulus obtained by fitting the 0%–2% strain data; (b) Poisson's ratio obtained by fitting the 0%–2% strain data.

particularly bond breakage and structural failure. Compared with ReaxFF, MLFF provides results that are closer to the DFT calculations in the simulations. This capability offers a new approach for large-scale simulations with DFT-level accuracy. Unlike traditional force fields, such as CVFF and ReaxFF, MLFF is optimized directly from DFT-based data, reducing human bias and offering broader applicability, positioning MLFF as a valuable tool for predictive simulations of material performance.

Bond Dissociation Energy

Nearly all the chemical reactions of organic compounds involve the breaking and formation of covalent bonds. Consequently, BDE is essential for understanding polymer durability, reactivity, and performance under mechanical or thermal stress.^[83,84] Accurate BDE prediction is crucial for evaluating polymer stability in various environments, particularly when a material is subjected to high temperatures or mechanical deformation.

To evaluate the performance of the MLFF in predicting BDEs, we selected several representative chemical bonds and compared their dissociation energies with those obtained from DFT calculations, which are considered the gold standard in high-accuracy predictions. Unlike CVFF, which relies on pre-determined bond parameters, MLFF is trained on QM datasets and is capable of simulating the bond dissociation process dynamically under a range of conditions, including varying temperatures and pressures. This flexibility enables a more detailed representation of bond-breaking behaviors, especially in complex non-equilibrium reaction environments.

In this study, BDE is defined as the standard energy change of the following fission: $AB \rightarrow A + B$. The BDE at 0 K, denoted by $D(A-B)$, is usually derived from the equation $D(A-B) = E(A) + E(B) - E(AB)$. As shown in Fig. 10, the MLFF results exhibit excellent agreement with DFT data, with a MAE of 7.8 kcal/mol across the six typical chemical bonds examined. These findings not only confirm the accuracy of the MLFF, but also underscore its potential for high-fidelity BDE prediction.

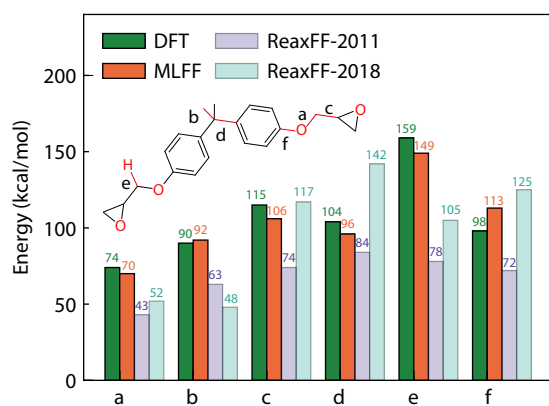


Fig. 10 Dissociation energies of the typical bonds.

In addition, we compared the BDE predictions made using ReaxFF. The results show that the BDE predicted by MLFF is closer to the DFT values, whereas both ReaxFF-2011 and ReaxFF-2018 exhibit significant deviations from the DFT. The differences between the versions of ReaxFF further indicate that the applicability of classical force fields is highly dependent

on the parameterized system; therefore, system-specific analysis should be performed prior to use.

CONCLUSIONS

In summary, this study developed an MLFF capable of accurately simulating the thermomechanical properties of the E51/IPDA epoxy-amine system. By leveraging QM training datasets and advanced learning algorithms, the proposed MLFF achieves precise predictions of key characteristics including RDFs, T_g , Young's modulus, Poisson's ratio, and BDEs. While conventional force fields such as CVFF and ReaxFF maintain their utility, with CVFF demonstrating superior computational efficiency and ReaxFF offering broader applicability through extensive parametrization, MLFF distinguishes itself through its data-driven approach. The incorporation of large-scale DFT training data enables a more accurate characterization of intermolecular interactions, yielding simulation results that closely align with the DFT-level accuracy. This capability establishes the MLFF as a promising methodology for large-scale simulations requiring quantum-mechanical precision.

The autonomous learning capacity of MLFF, derived from high-fidelity DFT datasets, significantly reduces the human-induced biases inherent in traditional force-field parameterization. However, it should be emphasized that the current validation is limited to the selection of performance metrics within this specific polymer system. Future work must address three critical aspects: (1) comprehensive validation across diverse polymer behaviors, (2) extension of the framework to broader polymer classes, and (3) systematic refinement of the model architecture to capture the intricate polymer dynamics. With continued advancements in machine learning architectures and force field optimization, MLFF has substantial potential to revolutionize computational material design, particularly in the development of next-generation polymeric materials.

Conflict of Interests

The authors declare no interest conflict.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://doi.org/10.1007/s10118-025-3389-4>.

Data Availability Statement

The related data supporting the findings of this study are available from the corresponding author upon reasonable request. Author's contact information: duank_1128@nudt.edu.cn.

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