REACTIVITY OF EPOXY RESINS AT THE NANOSCALE

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Abstract

Epoxy resins are heavily used in the field of fiber reinforced polymer composites as they generally show high stiffness and strength. However, combining these two properties with toughness is still highly challenging and therefore motivates continuous research both from applied and fundamental aspects. Such goal can only be reached if the fundamental mechanisms controlling the final properties of the resin are well understood. Nowadays, nanoscale simulation techniques have become effective approaches to complement high-tech experiments and offer an alternative route to understand the properties of complex systems. The objective of this work is to combine molecular dynamics simulations using the reactive force field ReaxFF and the transition path sampling methodology to better describe the dynamics of the curing process. In this study, the potential energy surfaces representative of the chemical reactions characterizing a curing process were determined. The obtained surface gave clear indications of the possible existence of optimized transition paths with lower activation energies and thus more plausible reaction mechanisms. Simulations are not limited to epoxy and can be extended to other thermosets and more broadly to any kind of polymers with the objective to further develop models to engineer polymer composite materials at the nanoscale.

1. Introduction

Among the various simulation techniques developed over the past half-century, molecular dynamics (MD) has gained popularity thanks to both its simple principle, solving the second law of Newton for atoms, and its efficiency in tackling a wide variety of problems. However for highly reactive molecular systems, the usage of standard MD together with fixed bonding force fields is not appropriate. The force field ReaxFF [1] offers an alternative route by considering possible formation and breakage of covalent bonds during the simulation, a requirement to model any crosslinking process. Odegard and al. [2] first modelled an EPON 862/DETDA system combining a classical distance criterion to model curing and a ReaxFF parameter set to predict the mechanical response. Seveno and Van Duin have also recently shown, using a different parameter set [3] that the formation of a crosslinked TGMDA/M-MIPA system can be modelled directly from monomers [4] (Figure 1). Primary amines react with the epoxy rings to form secondary amines, which are themselves converted into tertiary amines. The autocatalytic reaction between newly formed hydroxyl groups (created when amines react with an epoxy ring) and epoxy rings is also modelled, and competes with the non-catalytic reactions between the amines and epoxy rings. However, in this study the reactants had to overcome a steep energy barrier of typically 40 to 60 kcal/mol, 4 times higher than the experimental values obtained by Differential Scanning Calorimetry (Table 1). The chemical reactions can thus be

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considered as rare events as the probability to observe them is very small on the molecular time scale. In other words, the reaction cannot occur spontaneously within the timescale of a classical molecular dynamics simulation.

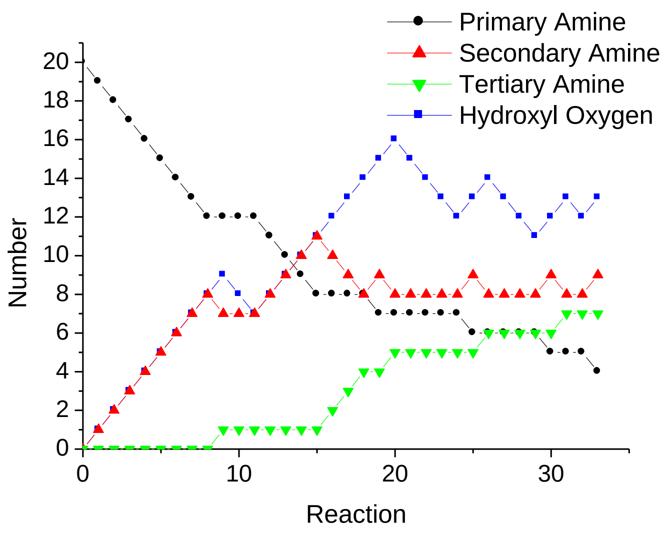

Figure 1. Dynamics of the curing process for a TGMDA/M-MIPA system [4].

Simulation of rare events with transition path sampling (TPS) has successfully been applied to a wide range of physical chemistry phenomena such as crystallization, catalysis, complex fluids, catalysis [5] but not yet to crosslinking of thermosets. In this study, the implementation of TPS permitted sampling of the energy landscapes associated with the chemical reactions and testing the existence of optimized transition paths with lower activation energies.

Table 1. Activation energies for different epoxy systems.

System	*Activation Energy* (kcal/mol)	*Technique*
TGAP, DGEBA, TGDDM, etc./ DDS, DETDA, etc.	11.0-18.0 (Primary amine) 9.1-19.6 (Secondary amine)	DSC [6]
DGEBA/DDM & DGEBA/DDS	11.1-11.3	DSC [7]
DGEBA/DDS	14.6	DSC [8]
DGEBA/EDA, PB2, PB4	13.2-14.1	DSC [9]
DGEBA, DGEBF, TGDDM/MPDA, DDS, DETA	31.8-43.8	Semi-empirical QM [10]

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2. Materials

Tetraglycidyl-4,4’-methylenedianiline (TGMDA) tetrafunctional epoxide and an aromatic diamine (hardener), 4,4'-methylenebis(2-isopropyl-6-methylaniline) (M-MIPA) (Figure 2) were selected as these monomers are amongst others precursors of the HexFlow® RTM6 resin (Hexcel) developed to fulfil the requirements of the aerospace industries in Resin Transfer Moulding (RTM). Also, with 4 reactive moieties (epoxy rings), TGMDA is a highly reactive monomer, which makes it suitable to be tested in reactive nanoscale simulations. The presence of water was also considered as it can act as a potential catalyst lowering the activation energies.

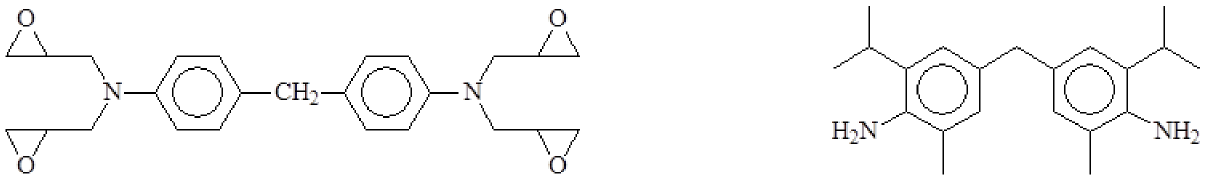

Figure 2. Chemical formulae of the TGMDA epoxy (left side) and M-MIPA hardener precursors (right side).

2. Computational method & Results

2.1. Reactive molecular dynamics

The method consists of generating dynamical trajectories of a molecular system by applying Newton's second law of motion to each atom. The parameter set of Monti et al. [3] was used to model the interactions between the atoms. The velocities and positions of the atoms were calculated from successive integrations via a velocity Verlet algorithm. The time step for the integration was set to 0.25 fs and restart files were saved every 2.5 fs. The temperature was fixed to 500 K and controlled by a Nose-Hoover thermostat. The successive positions of the atoms were generated by the LAMMPS code [11]. The first step requires to generate an initial reaction path starting with two reactants, one TGMDA and one M-MIPA molecule (state A) and ending with a product generated by the reaction between a primary amine group of the M-MIPA molecule and an epoxy ring of the TGMDA molecule (state B). The reaction had to be driven by restraining the distances between the carbon and oxygen and the nitrogen and hydrogen of respectively the epoxy and amine groups (Figure 3). When the distances between the atoms are small enough, the reactive force field is able to model correctly the reactions, which then occur over a few time steps. The proton is first transferred from the nitrogen to the oxygen, followed by the opening of the epoxy ring and finally the formation of a bond between the carbon and nitrogen atoms. Bringing the carbon and nitrogen atoms and the hydrogen and oxygen atoms close to each other respectively cost 22 and 60 kcal/mol whereas the proton transfer lowers the energy by 22 kcal/mol, i.e. the overall activation energy is 60 kcal/mol (Figure 4). The same procedure with an additional water molecule shows a more favorable activation energy of 33 kcal/mol. The connectivity (fix reax/c/bonds) and species (fix reax/c/species) tables available in LAMMPS were analyzed (via TCL scripts) to check the dynamics of the bonds and the completion of the reactions.

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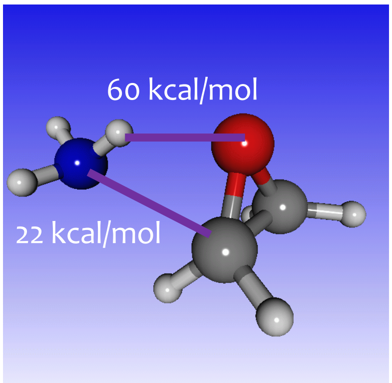

Figure 3. Amine and epoxy reactive groups. The full magenta lines illustrate the additional restraints needed to drive the reaction.

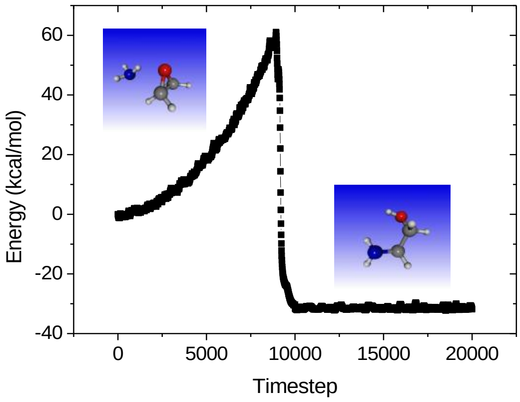

Figure 4. Energy barrier associated with the reaction between a primary amine and an epoxy ring reactive groups.

This initial (biased) simulation was subsequently used as a seed to generate new paths between states A and B with this time no restraint on the distances between the atoms. The procedure consists of restarting the simulation at times just before and after the reaction took place with the initial atom velocities reinitialized. The molecules can thus sample configurations not accessible when the distances between the atoms are restrained. To check if a simulation can reach state A starting from state B (backward direction), the initial velocities were reversed. The combination of the simulations going in the forward and backward directions permits to check if a new simulation is spontaneously able to start from state A and end up in state B following paths energetically more favorable (Figure 5). This is considered as a successful simulation. For every “seed simulation”, 200 restart files were selected and tested 100 times (in both the forward and backward directions), i.e. up to 20000 unconstrained simulations could be utilized to scrutinize the reaction paths and generate the potential energy surface (PES) to identify possible lower activation energy paths. In practice, for every simulation, every 10 time steps, the distances between the atoms of the reactive groups and the potential energy of the molecular system were saved and its state (A or B) checked.

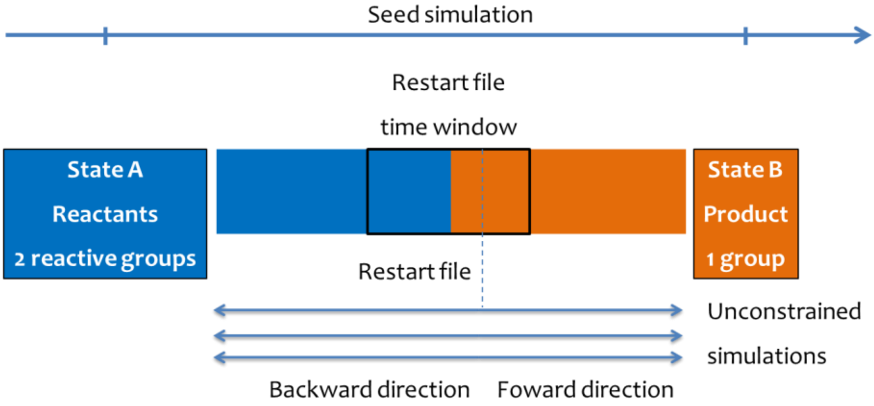

Figure 5. Schematic illustration of the simulation methodology.

Figure 6 illustrates the regions of the conformational space leading to either a completed or incompleted reaction. It is clear that the primary amine/epoxy ring reaction can only occur in a restricted area limited by distances between the carbon and nitrogen atoms (C-N bond) and the oxygen and hydrogen atoms (O-H bond) of respectively 1.95 Å and 1.35 Å. These distances represent a

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stringent condition which could explain why a spontaneous reaction is not modelled by classical MD. From an energetic point of view, Figure 7 confirms that the area modelling the reaction is difficult to reach as an energy barrier located between 1.65 Å and 1.95 Å for the C-N bond and spanning over the O-H bond has to be overcome. If the "seed simulation" can anyway move along this path thanks to the restrains on the C-N and O-H distances (black full line in Figure 7), the unconstrained simulations only rarely end up in this area starting from state A. Only ballistic approaches (magenta full line in Figure 7) are eventually successful.

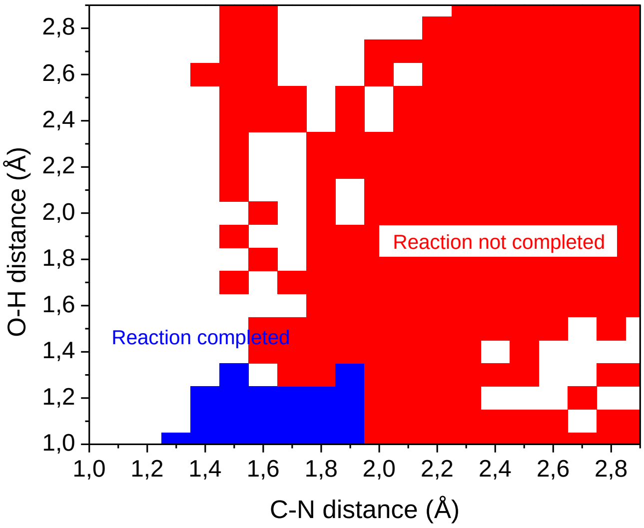

Figure 6. Conformational space showing the regions where the reaction is completed (in blue) and not completed (in red).

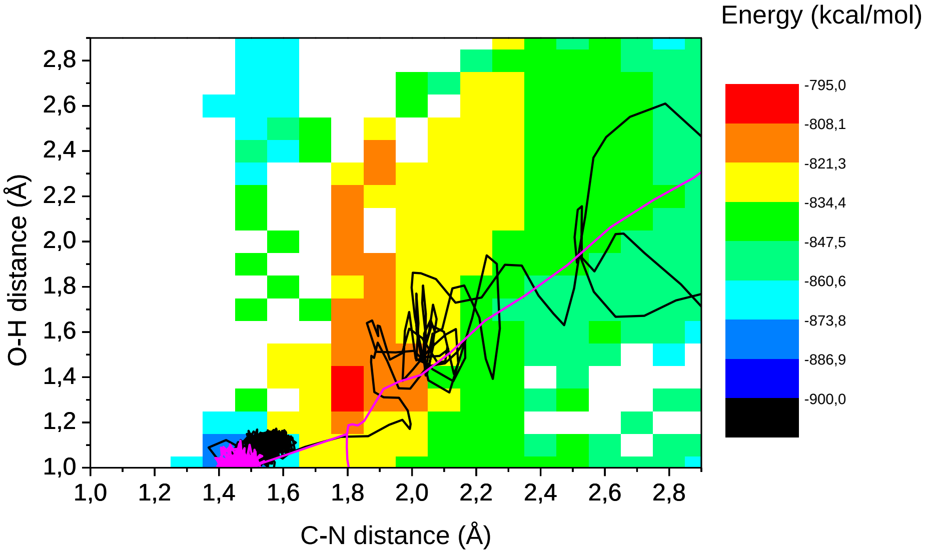

Figure 7. Potential energy surface of a TGMDA/M-MIPA system at 500K. The black line illustrates the path followed by the two reactants for a simulation with constrained distances. The magenta line exemplifies a ballistic approach obtained for a simulation without constrained distances.

The same procedure was implemented with a water molecule as it was shown to lower the activation energy, while the potential energy landscape remains almost identical. Even though sampling the

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conformational space starting from a unique path permitted to partially unravel the complexity of the primary amine/epoxy ring, multiple unbiased paths should be tested to improve our view on this process. This is the objective of the transition path sampling technique.

2.2. Transition path sampling

In the frame of this study, a basic TPS methodology was applied to the epoxy system described above. TPS smartly combines MD and Monte-Carlo (MC) simulations to predict the kinetics of rare events at the nanoscale. If MD simulations are fully deterministic, classical MC simulations are based on a stochastic principle aiming at predicting the equilibrium configurations of a molecular system. Similarly to MD, one first has to prescribe the initial positions of atoms. They are then randomly displaced, contrary to MD, to generate a new configuration. If the energy difference ΔE (calculated via the force field) between the novel and previous configurations is negative then the displacement is accepted. If ΔE is positive, it is accepted following a probability distribution characterized by the Boltzmann factor $e^{-\Delta E/k_B T}$ with k_B the Boltzmann constant and T the temperature (K). Iterating over the accepted configurations, equilibrium configurations showing the lowest potential energies are progressively predicted. Due to the randomness of the atomic displacements, unphysical intermediate configurations can be generated offering the opportunity to the molecular system to escape from a local minimum of the PES to reach after a few iterations a more stable configuration and hypothetically the global energy minimum. This is a clear advantage compared to MD which can not model transitions from low energy to high energy configurations. However the transient regime to reach equilibrium is not physical for MC and therefore not useable. It is for MD.
A TPS methodology, based on the same principle, was developed to identify optimized paths linking two basins of attraction characterized by the states A and B. A "seed simulation" was first performed as described in section 2.1. A restart file was then randomly selected and simulations restarted in the forward and backward directions. A successful path being identified as a simulation connecting without restrain state A and B. Such simulation is then considered as the novel "seed" simulation from which a restart file is again randomly selected and simulations restarted in both directions. This procedure is repeated until two consecutive successful paths do not show significant differences (Figure 8). Here, a maximum of 500 paths (100 trials per path) were tested per iteration for a maximum of 20 iterations.

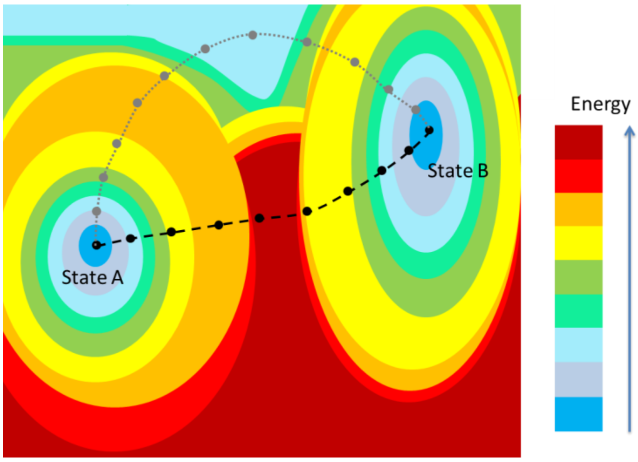

Figure 8. Schematics of a PES showing an initial path (black dashed line) and an optimized path obtained via TPS (gray dotted line) between two basins of attraction.

The TPS procedure did generate several accepted paths, but the acceptance ratio was low, and almost all successful trajectories were initiated from the same region. This indicates that the path ensemble is

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very hard to relax. This is also reflected in the committor *p*, the probability to reach state B, as a function of the time step (restart file) for a single TPS trajectory. Before the transition state, i.e. p=0.5, the simulation has a tendency to return to state A (p<0.5) whereas after the transition, it most likely reaches state B (p>0.5). For the TGMDA/M-MIPA system, we computed the committor by running 100 simulations from each restart file in the trajectories, with random initial velocities according to the Maxwell-Boltzmann distribution. The committor was estimated as the fraction of trajectories that reach B instead of A. From Figure 9, it is clear that the committor remains either equal to 0 or to 1 except very close to the transition state. This means that the part of the trajectory where a successful path could be generated is very short, compared to the total length, i.e. the probability to predict spontaneously the location of the curing reaction is very low (Figure 9). The role of water, not modelled here, may greatly influence the reaction paths and explain the discrepancies between experimental and modelling results.

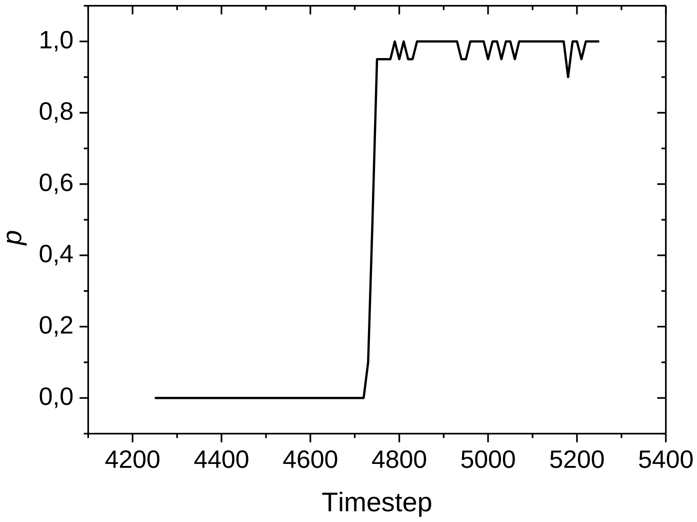

Figure 9. Probability of reaching state B versus time step.

4. Conclusions

The objectives of this study were mainly to integrate the transition path sampling technique in the current simulations modelling the curing process of epoxy via LAMMPS and the reactive force field ReaxFF and to use this new numerical tool to shed light on the reactivity of epoxy resins at the nanoscale. If combining MD and the ReaxFF force field is relatively straightforward using the LAMMPS software, the integration of the TPS technique required much more effort. In practice, it consisted of writing TCL scripts enabling the restart of MD simulations in the forward and backward directions to check if the desired states (A for reactants and B for products) are obtained, and to calculate the activation energies (in both directions) to select appropriate novel paths. The results of the simulations can either be illustrated by the probability of reaching state B as a function of time (committor) or in the form of a PES imaging the existence of peaks and valleys of energy. The results indicated that the crosslinking reactions as they are modelled by ReaxFF require to overcome sharp activation energy peaks, which can hardly be lowered. This conclusion still has to be confirmed as the PES was not entirely sampled by the simulations. Unexplored regions still have to be characterized as well as the effect of water possibly acting as a catalyst. These prospective works are ongoing as well as the implementation of the Nudged Elastic Band (NEB) technique [12], [13] as an alternative methodology to the basic TPS methodology here proposed.

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References

[1] A. C. T. van Duin, S. Dasgupta, F. Lorant, and W. a. Goddard, “ReaxFF: A Reactive Force Field for Hydrocarbons,” *J. Phys. Chem. A*, vol. 105, no. 41, pp. 9396–9409, Oct. 2001.

[2] G. M. Odegard, B. D. Jensen, S. Gowtham, J. Wu, J. He, and Z. Zhang, “Predicting Mechanical Response of Crosslinked Epoxy using ReaxFF,” *Chem. Phys. Lett.*, Nov. 2013.

[3] S. Monti, A. Corozzi, P. Fristrup, K. L. Joshi, Y. K. Shin, P. Oelschlaeger, A. C. T. van Duin, and V. Barone, “Exploring the conformational and reactive dynamics of biomolecules in solution using an extended version of the glycine reactive force field.,” *Phys. Chem. Chem. Phys.*, vol. 15, no. 36, pp. 15062–77, Sep. 2013.

[4] D. Seveno and A. van Duin, “Curing of epoxy resins at the nanoscale,” in *20th International Conference on Composite Materials; Copenhagen*, 2015.

[5] P. G. Bolhuis, C. Dellago, P. L. Geissler, and D. Chandler, “Transition path sampling: Throwing ropes over mountains in the dark,” *J. Phys. Condens. Matter*, vol. 12, no. 8 A, 2000.

[6] H. Liu, A. Uhlherr, R. J. Varley, and M. K. Bannister, “Influence of substituents on the kinetics of epoxy/aromatic diamine resin systems,” *J. Polym. Sci. Part A Polym. Chem.*, vol. 42, no. 13, pp. 3143–3156, Jul. 2004.

[7] M. L. M. Costa, L. L. C. Pardini, and M. C. M. Rezende, “Influence of aromatic amine hardeners in the cure kinetics of an epoxy resin used in advanced composites,” *Mater. Res.*, vol. 8, no. 1, pp. 65–70, 2005.

[8] J. Gonis, G. P. Simon, and W. D. Cook, “Cure properties of epoxies with varying chain length as studied by DSC,” *J. Appl. Polym. Sci.*, vol. 72, no. 11, pp. 1479–1488, 1999.

[9] J. Wan, C. Li, Z. Y. Bu, C. J. Xu, B. G. Li, and H. Fan, “A comparative study of epoxy resin cured with a linear diamine and a branched polyamine,” *Chem. Eng. J.*, vol. 188, pp. 160–172, 2012.

[10] T. Okabe, T. Takehara, K. Inose, N. Hirano, M. Nishikawa, and T. Uehara, “Curing reaction of epoxy resin composed of mixed base resin and curing agent: Experiments and molecular simulation,” *Polym. (United Kingdom)*, vol. 54, no. 17, pp. 4660–4668, 2013.

[11] S. Plimpton, “Fast Parallel Algorithms for Short-Range Molecular Dynamics,” *Journal of Computational Physics*, vol. 117, no. 1. pp. 1–19, 1995.

[12] V. Sundararaghavan and a. Kumar, “Molecular dynamics simulations of compressive yielding in cross-linked epoxies in the context of Argon theory,” *Int. J. Plast.*, vol. 47, pp. 111–125, Aug. 2013.

[13] Y. Tang, J. Zhou, C. Li, W. Chen, and X. Dai, “Theoretical Study of Epoxy Group Adsorption and Diffusion on Pristine, Defected Graphene Sheets,” *Integr. Ferroelectr.*, vol. 164, no. 1, pp. 112–121, 2015.

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