San Jose State University

# SJSU ScholarWorks

4-1-2024

# Simulation data for engineering graphene quantum dot epoxy nanocomposites using molecular dynamics

Prathamesh P. Deshpande
*San Jose State University*, prathamesh.deshpande@sjsu.edu

Ozgur Keles
*San Jose State University*, ozgur.keles@sjsu.edu

Follow this and additional works at: https://scholarworks.sjsu.edu/faculty_rsca

## Recommended Citation

Data Article

# Simulation data for engineering graphene quantum dot epoxy nanocomposites using molecular dynamics

Prathamesh P. Deshpande*, Ozgur Keles

*San Jose State University, 1 Washington Sq., San Jose, CA 95192, USA*

## ARTICLE INFO

## ABSTRACT

Graphene quantum dots (GQDs) were reported to fill the role of nanofillers that enhance composite properties. Detailed investigation of this nanofiller in composites is largely unexplored. To understand the fundamental mechanisms in play, this study uses molecular dynamics simulations to reveal the effects of GQDs on epoxy properties. Mechanical simulations were performed on three varying GQD chemistries which included a pristine GQD and 2 edge aminated GQDs with different degrees of functionalization (5.2 % and 7.6 %). These GQDs were separately inserted in a polymer matrix across five individual replicates. The nanocomposite mechanical properties were computed using uniaxial strain simulations to display the effect of embedded GQDs.

---

* Corresponding author.
  *E-mail address:* prathamesh.deshpande@sjsu.edu (P.P. Deshpande).
  *Social media:* @ppdeshpande257 (P.P. Deshpande)

Specifications Table

| | |
|---|---|
| Subject | Computational Mechanics, Computational Materials, Material Science |
| Specific subject area | Molecular Dynamics simulation of GQD-epoxy nanocomposites |
| Data format | Raw: LAMMPS trajectory, input scripts, and log files |
| | Analysed: stress-strain plots |
| Type of data | LAMMPS simulation and mechanical property plots |
| Data collection | Molecular dynamics simulations were performed on a computing cluster at San Jose State University using LAMMPS open-source software. The data was post-processed using custom python scripts to generate the mechanical property predictions. |
| Data source location | San Jose State University, San Jose, CA 95192 |
| Data accessibility | Repository name: Mendeley Data |
| | Data identification number: 10.17632/gmm7rfrsdt.1 |
| | Direct URL to data: https://data.mendeley.com/datasets/gmm7rfrsdt/1 |

## 1. Value of the Data

- The detailed simulation data provides structural evolution of the GQD-epoxy nanocomposite during mechanical deformation. Along with the atom trajectories, the stress-strain response is supplied to link the structure and the properties of nanocomposite models.
- Polymer scientists invested in GQD filled composites can gain substantial insight into the molecular behavior of the material. Also, other computational researchers benefit from the modeling methodology and analysis techniques.
- The data describes a generalized case and provides pathways to more complex modeling methods.

## 2. Background

Thermoset composites are notably used in different industries requiring high-performance materials. The polymer matrix is an amorphous material with low toughness which is usually supplemented with nanofillers. Nanofillers like GQDs have been shown to enhance the material properties of the matrix [1–4]. Recent studies have affirmed these claims for GQD-epoxy composites [5]. To fully understand the inherent mechanisms responsible for property enhancements, this study uses molecular dynamics to model the polymer-GQD nanocomposite. Various interactions were observed, and mechanical simulations were performed to see the effect of GQDs on the properties. The data generated in this study was used to establish the findings linking GQD chemistry to the output mechanical properties. The simulated data includes the entire workflow of modelling the GQD-epoxy nanocomposite right from the inception of individual monomeric components.

## 3. Data Description

The simulation data is distributed in four main directories for the four modelled material systems – epoxy, GQD-epoxy, 4N-GQD-epoxy, and 6N-GQD-epoxy. Each directory has several sub-directories which include LAMMPS files for a specific simulation. Table 1 details the description of all the sub-directories and Table 2 details the description of the files within the sub-directories.

**Table 1**

Directory data description for the four material systems.

| Directory name | Simulation Type | Simulation Details |
|---|---|---|
| step_1 | Monomer generation | Generating individual monomeric components using the IFF-R forcefield |
| step_2 | Bulk polymer at liquid density | Mixing the polymer components in a stoichiometric ratio and compressing the model to liquid density |
| step_3 | Annealing | Inserting the GQD and cooling the model from elevated temperature to cure temperature |
| step_4 | Crosslinking | Chemical crosslinking to form the polymer network |
| step_5 | Annealing | Cooling down the model from cure temperature to room temperature and relaxing the model |
| step_6 | Relaxation | Changing the forcefield from IFF-R to ReaxFF and equilibrating the model |
| step_7 | Tension | Apply strain to the simulation box in three principal directions (x-, y-, and z- axis) separately |

**Table 2**

File data description for the sub-directory contents.

| File Types | File Details |
|---|---|
| dump.* | LAMMPS trajectory |
| *.data | LAMMPS structure |
| in.* | LAMMPS input script |
| *.log or log.* | LAMMPS log |
| *.moltemp | reaction template |
| *.ecoeffs | reaction template coefficients |
| *.txt | reaction map |
| *.csv | stress-strain data |
| *.reax | ReaxFF forcefield file |

## 4. Experimental Design, Materials and Methods

The epoxy resin used in this study is the diglycidyl ether bisphenol F (DGEBF), sold commercially as EPON 862. The curing agent used in the diethyl toluene diamine (DETDA), sold commercially as Epikure W. The two molecules were modelled and mixed in a simulation box with the stoichiometric ratio of 2:1 using the IFF-R forcefield in LAMMPS software [6–8]. The selected stoichiometric ratio was selected to maximize the chemical crosslinking between the molecules during the virtual cure [9,10]. The mixture was multiplied to generate a larger model with the total atom count of 5616 atoms and the total molecule count of 144.

The initial density of the system was 0.09 – 0.10 g/cm$^3$. Before densifying the system, the molecules were allowed to mix by ramping the system temperature down from 600 K to 300 K over 100 picoseconds (ps). A Nose-Hoover thermostat [11–14] was used and the timestep was set to 1 femtosecond (fs). The simulation box was gradually densified by compression from all directions. The compression was simulated over 8 nanoseconds (ns) with the target density of 1.2 g/cm$^3$.

A virtual curing simulation was performed at 499 K over 1.5 ns using the REACTER tool within LAMMPS [15]. The simulated cure reaction is the two-step amine-epoxy reaction. Details on the curing simulation settings is described elsewhere [10]. To account for uncertainty of property prediction, five unique replicates were modelled. The average crosslink density between the five models was 81.77 $\pm$ 3.47%. Fig. 1 shows (a) the amine reaction and (b) amine content in a representative model and conversion during crosslinking simulations. Post-crosslinking, the models were annealed to promote optimal conformation of the newly formed network. The system temperature was ramped down from 600 K to 300 K with a constant cooling rate of 100 K/ns. Fig. 2 shows the temperature and density profile during the annealing simulation. Next, the system was equilibrated over 1 ns using a Nose-Hoover barostat and thermostat at 1 atm
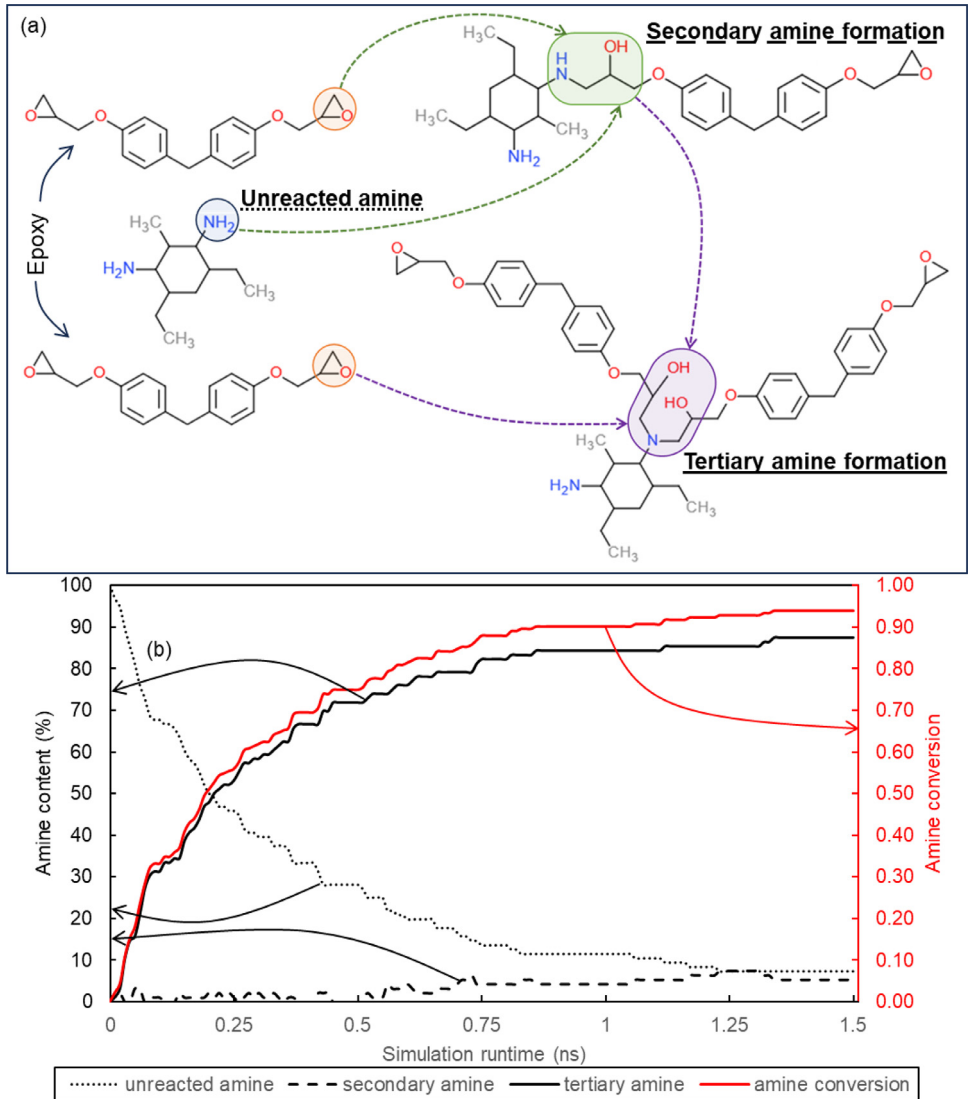
**Fig. 1.** (a) Epoxy-amine reaction pathway for a bisphenol-F epoxy (DGEBF) and diethyl toluene diamine (DETDA) and (b)amine content and conversion during the chemical crosslinking simulation in a representative model with 90 % crosslink density.

pressure and 300 K temperature respectively. Fig. 3(a) shows a representative MD model after full equilibration.

To perform the mechanical deformation simulations, the models were equilibrated by switching the forcefield parameters from IFF-R to ReaxFF [9,16]. This ReaxFF parameter set was chosen because of the accuracy of density prediction in various hydrocarbon-based materials [17]. As established by Odegard et al. [6], accurate density prediction is essential for capturing the corresponding mechanical response of the material. The equilibrated models were then deformed in the three directions (*x*-, *y*-, and *z*- direction). To allow the Poisson contraction, an NPT ensemble was used to relax the lateral directions. The maximum applied strain was set at 10% with the
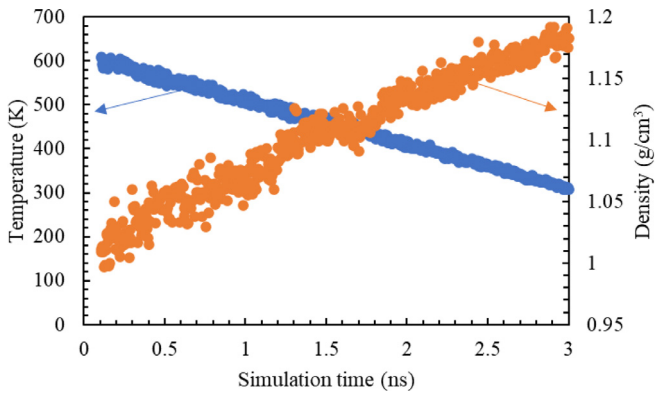
**Fig. 2.** Temperature and density profile during annealing simulation.
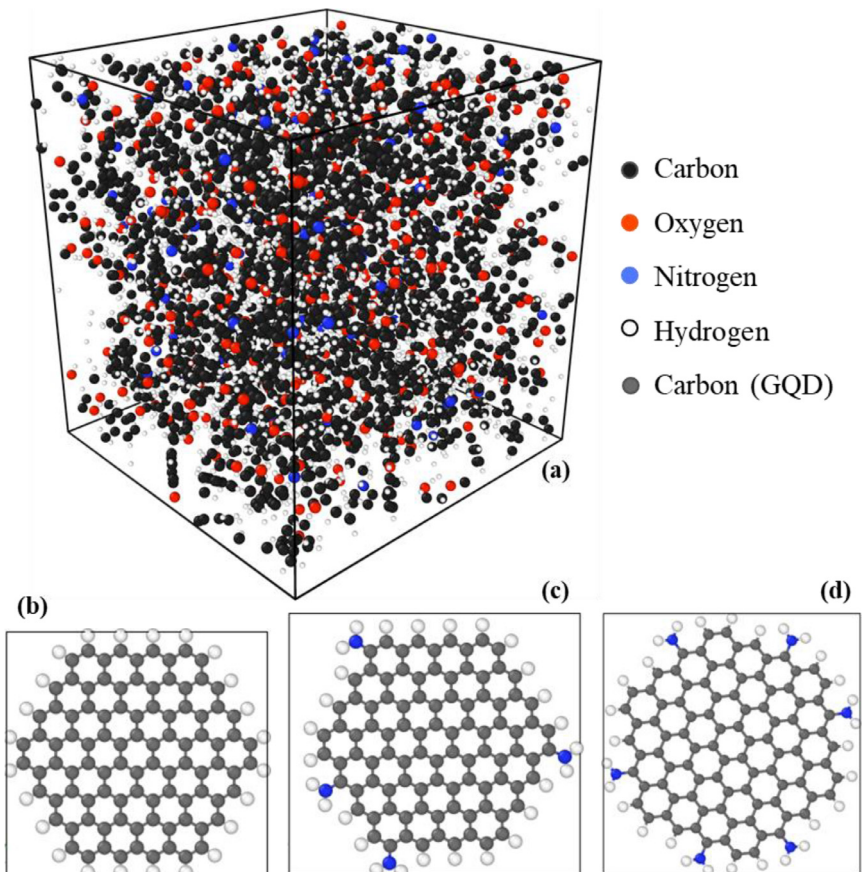


**Fig. 3.** (a) Representative equilibrated epoxy model. (b) Isolated GQD model before integration (Top view), (c) Isolated 4N-GQD model before integration (Top view), and (c) Isolated 6N-GQD model before integration (Top view).

strain rate of $2 \times 10^8$ /s and 0.1 fs timestep. The stress-strain data was then analysed to extract the Young's modulus and the yield strength of the material. A piecewise multi-linear curve fitting technique was used to extract the Young's modulus, Poisson's ratio and establish a yield point on the stress-strain curve.

A pristine GQD was modelled using an in-house Python script and LAMMPS. The edge carbon atoms were terminated with hydrogen atoms. The dimensions of the modelled GQD were 1.9 nm $\times$ 1.8 nm in zigzag configuration. Fig. 3(b) shows the GQD structure modelled in LAMMPS. The model contains 5616 epoxy atoms and 120 GQD atoms. The modelled GQD was combined with epoxy and annealed as demonstrated by Deshpande et al. [18]. The annealing simulation settings and rest of successive simulations were identical to the neat epoxy simulation described in previous section. Five replicates were modelled to account for uncertainty in property prediction.

The functionalized GQD was modelled using an in-house Python script and LAMMPS. The functional group of choice was the primary amine ($NH_2$) and were randomly distributed on the edge of the GQD. Two f-GQD were modelled with different amount of amine groups. For the first sub-system (4N-GQD-epoxy), the total amount of functional groups accounted for 5.2% of the total mass of the GQD. The chosen structure is shown in Fig. 3(c), the structure has four primary amine groups and 2.1 $\times$ 1.9 nm in dimensions. For the second sub-system (6N-GQD-epoxy), the total amount of functional groups accounted for 7.6% of the total mass of the GQD. Fig. 3(d) shows the structure with six primary amine groups with dimensions 1.8 $\times$ 1.9 nm. As described in the previous section, the f-GQD and epoxy models were combined using LAMMPS and annealed. The model consisted of 5616 epoxy atoms and 128 f-GQD atoms. Post-annealing, the model was subjected to crosslinking. With the presence of the functional groups, a secondary chemical reaction was performed where the epoxy molecules reacted with the primary amines on the GQD. This secondary reaction is identical to the reaction occurring within the epoxy material due to similar chemistry.

## Limitations

Not applicable.

## Ethics Statement

The authors have read and follow the ethical requirements for publication in Data in Brief and confirm that the current work does not involve human subjects, animal experiments, or any data collected from social media platforms.

## Data Availability

Molecular Dynamics Modeling of Graphene Quantum Dot Epoxy Nanocomposite To Predict Physio-Mechanical Properties (Original data) (Mendeley Data)

## CRediT Author Statement

**Prathamesh P. Deshpande:** Conceptualization, Methodology, Software, Validation, Investigation, Resources, Data curation, Writing – original draft, Writing – review & editing, Visualization; **Ozgur Keles:** Conceptualization, Methodology, Investigation, Resources, Writing – review & editing, Supervision, Project administration, Funding acquisition.

## Acknowledgements

## Declaration of Competing 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.

## References

[1] N. Gobi, D. Vijayakumar, O. Keles, F. Erogbogbo, Infusion of graphene quantum dots to create stronger, tougher, and brighter polymer composites, ACS Omega 2 (8) (2017) 4356–4362.

[2] A. Navidfar, M.I. Peker, E. Budak, C. Unlu, L. Trabzon, Carbon quantum dots enhanced graphene/carbon nanotubes polyurethane hybrid nanocomposites, Composites Part B (2022) 247.

[3] S. Riaz, S.-J. Park, A comparative study on nanoinclusion effect of MoS2 nanosheets and MoS2 quantum dots on fracture toughness and interfacial properties of epoxy composites, Composites Part A 146 (2021) 106419.

[4] J.R. Seibert, Ö. Keleş, J. Wang, F. Erogbogbo, Infusion of graphene quantum dots to modulate thermal conductivity and dynamic mechanical properties of polymers, Polymer 185 (2019) 121988.

[5] B. Karimi, B. Ramezanzadeh, A comparative study on the effects of ultrathin luminescent graphene oxide quantum dot (GOQD) and graphene oxide (GO) nanosheets on the interfacial interactions and mechanical properties of an epoxy composite, J. Colloid Interface Sci. 493 (2017) 62–76.

[6] G.M. Odegard, S.U. Patil, P.P. Deshpande, K. Kanhaiya, J.J. Winetrout, H. Heinz, S.P. Shah, M. Maiaru, Molecular dynamics modeling of epoxy resins using the reactive interface force field, Macromolecules 54 (21) (2021) 9815–9824.

[7] J.J. Winetrout, K. Kanhaiya, G. Sachdeva, R. Pandey, B. Damirchi, A. van Duin, G. Odegard, H. Heinz, arXiv preprint, 2021.

[8] A.P. Thompson, H.M. Aktulga, R. Berger, D.S. Bolintineanu, W.M. Brown, P.S. Crozier, P.J. in 't Veld, A. Kohlmeyer, S.G. Moore, T.D. Nguyen, R. Shan, M.J. Stevens, J. Tranchida, C. Trott, S.J. Plimpton, LAMMPS - a flexible simulation tool for particle-based materials modeling at the atomic, meso, and continuum scales, Comput. Phys. Commun. 271 (2022) 108171.

[9] M.S. Radue, B.D. Jensen, S. Gowtham, D.R. Klimek-McDonald, J.A. King, G.M. Odegard, Comparing the mechanical response of di-, tri-, and tetra-functional resin epoxies with reactive molecular dynamics, J. Polym. Sci. B 56 (3) (2018) 255–264.

[10] S.U. Patil, S.P. Shah, M. Olaya, P.P. Deshpande, M. Maiaru, G.M. Odegard, Reactive molecular dynamics simulation of epoxy for the full cross-linking process, ACS Appl. Polym. Mater. 3 (11) (2024) 5788–5797.

[11] G.J. Martyna, D.J. Tobias, M.L. Klein, Constant pressure molecular dynamics algorithms, J. Chem. Phys. 101 (5) (1994) 4177–4189.

[12] M.E. Tuckerman, J. Alejandre, R. López-Rendón, A.L. Jochim, G.J. Martyna, A Liouville-operator derived measure-preserving integrator for molecular dynamics simulations in the isothermal–isobaric ensemble, J. Phys. A 39 (19) (2006) 5629.

[13] M. Parrinello, A. Rahman, Polymorphic transitions in single crystals: a new molecular dynamics method, J. Appl. Phys. 52 (12) (1981) 7182–7190.

[14] W. Shinoda, M. Shiga, M. Mikami, Rapid estimation of elastic constants by molecular dynamics simulation under constant stress, Phys. Rev. B 69 (13) (2004) 134103.

[15] J.R. Gissinger, B.D. Jensen, K.E. Wise, REACTER: a heuristic method for reactive molecular dynamics, Macromolecules 53 (22) (2020) 9953–9961.

[16] G.M. Odegard, B.D. Jensen, S. Gowtham, J. Wu, J. He, Z. Zhang, Predicting mechanical response of crosslinked epoxy using ReaxFF, Chem. Phys. Lett. 591 (2014) 175–178.

[17] W. Zhang, A.C.T. van Duin, Improvement of the ReaxFF description for functionalized hydrocarbon/water weak interactions in the condensed phase, J. Phys. Chem. B 122 (14) (2018) 4083–4092.

[18] P.P. Deshpande, M.S. Radue, P. Gaikwad, S. Bamane, S.U. Patil, W.A. Pisani, G.M. Odegard, Prediction of the interfacial properties of high-performance polymers and flattened CNT-reinforced composites using molecular dynamics, Langmuir 37 (39) (2021) 11526–11534.