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Mechanical behavior of graphene quantum dot epoxy nanocomposites: A molecular dynamics study

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ABSTRACT

Quantum dot fillers were reported to enhance stiffness, yield strength, and toughness of polymers. However, the underlying mechanisms for these enhancements are unclear. In this study, for the first time, molecular dynamics simulations were performed to reveal the effects of graphene quantum dots (GQDs) on epoxy properties. Mechanical simulations revealed that addition of a single-layer graphene quantum dot with six reactive amine groups enhanced the epoxy yield strength by 17% and stiffness by 6%; whereas pristine GQDs reduced the strength by 6% and stiffness by 10%. The results show the importance of surface chemistry of GQDs towards the intelligent design of strong, tough, and multifunctional nanocomposites.

1. Introduction

Thermosets are used in various industries because they exhibit higher stiffness, strength, and fire resistance compared to thermoplastics [1]. Moreover, fiber reinforced thermoset composites dominate structural applications demanding high strength-stiffness and low density [2]. Thermosets have a highly crosslinked molecular structure, which causes low toughness, e.g., epoxy $K_{IC} < 1\ \text{MPa}.\sqrt{\text{m}}$ [3]. To enhance the properties of epoxies, many different fillers (graphene, clay, rubber, others) have been used [4–6]. Yet, the effects of these fillers are often limited due to poor bonding, agglomeration, voids, misalignment, and waviness [7,8]. The size scale of the common fillers is generally orders of magnitude larger than epoxy molecules of 1–2 nm size.

For perspective, epoxy-composites with clay fillers (~5 wt%, d = 10–20 μm) reported a peak increase of ~38 % and ~42 % in tensile modulus and strength respectively [6]. Particulate rubber (<10 wt%, d = ~90 nm) lowers the stiffness of the epoxy by 3–10 % and strength by 2–20 % [9,10]. The carbon-based nanofillers have displayed higher increments in the tensile properties (2–30 % in stiffness and 10–60 % in strength) of the epoxy with relatively lower nano-reinforcement (<5 wt %, d(GNP/GO) = ~1–40 μm, d(CNT) = ~1–140 nm) [4,11]. On the other hand, two-dimensional quantum dots (QDs) are also used as fillers [12–14]. QDs are nanoparticles smaller than 20 nm. QDs main advantages over larger fillers are: (1) their negligible effect on the viscosity of thermoset resins, (2) high ratio of surface functional groups to the volume, and (3) optical functionalization that enables strain sensing [15–17]. QDs' small size with covalent integration enhances thermal conductivity better than graphene nano platelets for a given weight percent [15].

Recent studies also showed that QDs with functional groups enhance mechanical properties of thermosets [12–14]. For example, addition of 2.5 wt% graphene quantum dots (GQDs, 16 nm average diameter) enhanced the strength of epoxy by 125 % and elastic modulus by 153 % [12]. Addition of ~0.1 wt% graphene oxide quantum dots (5–6 nm in diameter) enhanced epoxy strength by 127 % and elastic modulus by 11 % [13]. Moreover, addition of 0.2 wt% molybdenum sulfide QDs (average diameter of 2.3 nm) enhanced epoxy strength by 66 %, elastic modulus by 6 %, and fracture toughness by 81 % [14]. The reasons for these stiffness, strength, and toughness enhancements with the addition of QDs are unclear. At nanoscale, molecular dynamics (MD) simulations provide a platform to explore the molecular mechanisms responsible for stiffening and strengthening [18,19]. Therefore, we created the first MD framework to simulate synthesis of GQD-epoxy nanocomposites and investigate the nano-scale structure–mechanical property relationships.

2. Molecular modeling

The Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) software package was used for performing all the MD simulations [20]. We used conventional CPU based simulations with the Reactive Interface Forcefield (IFF-R) to crosslink (curing) and GPU-accelerated simulations with the Reactive Forcefield (ReaxFF) to

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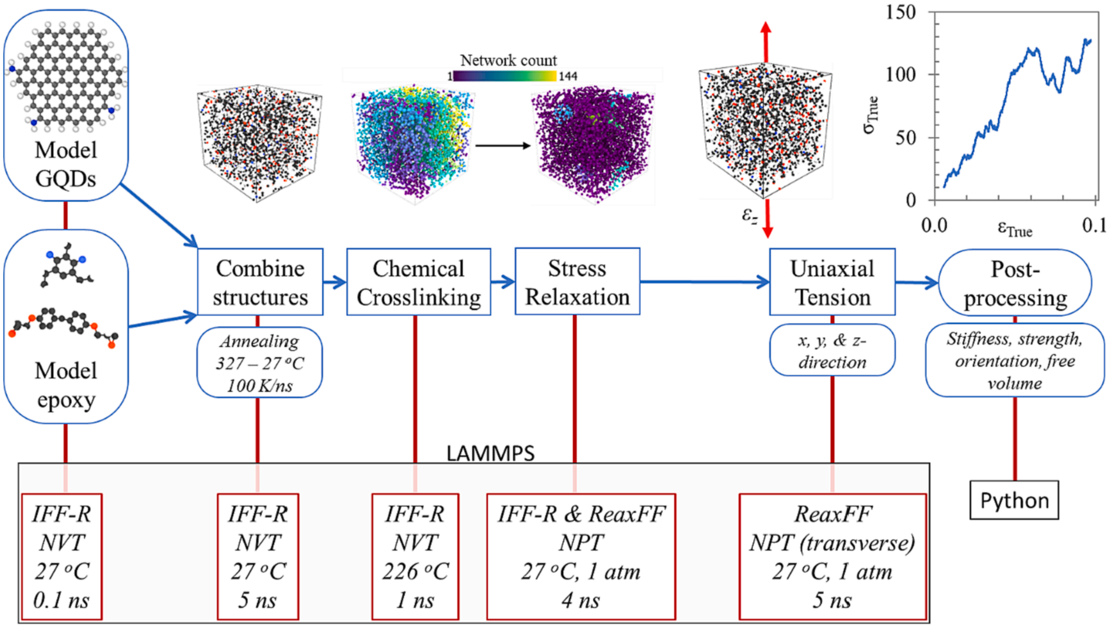

Fig. 1. MD modeling framework for neat epoxy resins and their GQD-nanocomposites.

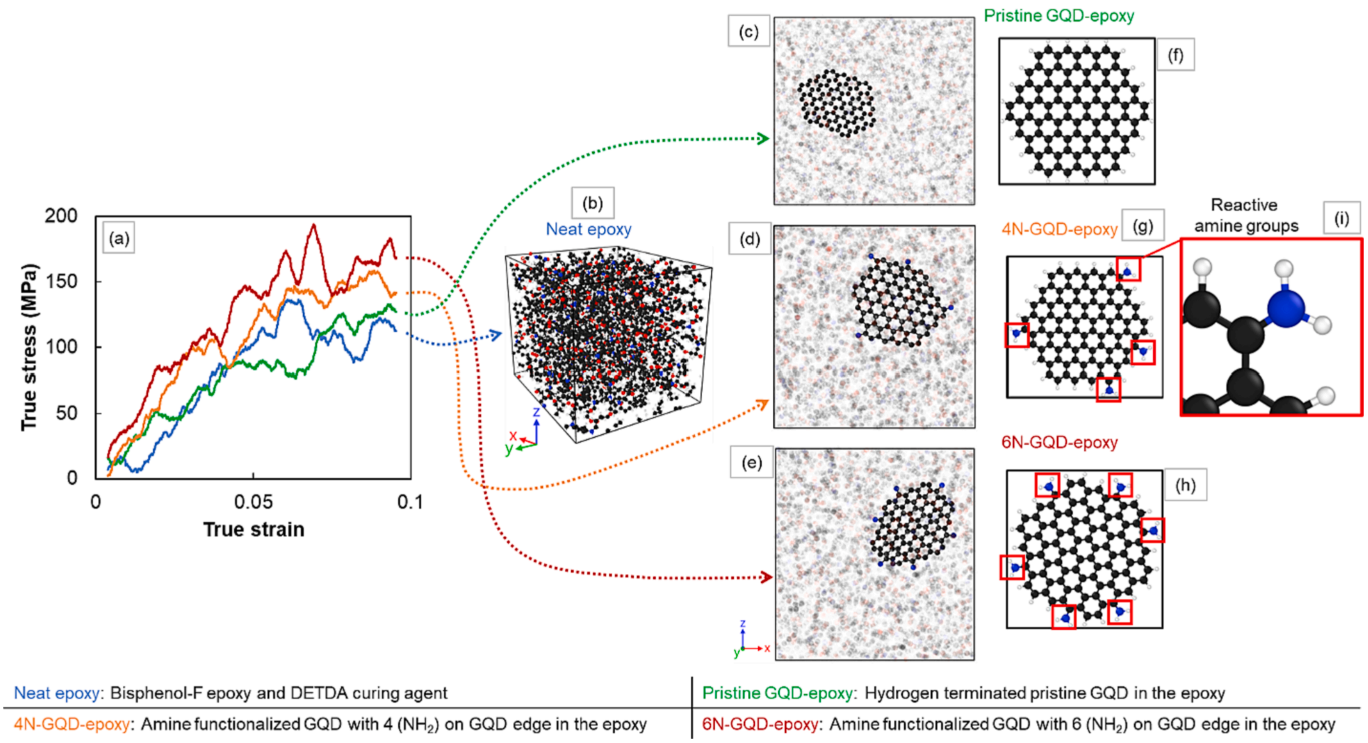

Fig. 2. (a) Representative stress–strain curves for the four different structures. MD models of (b) neat epoxy, (c) pristine GQD-epoxy, (d) 4N-GQD-epoxy, and (e) 6N-GQD-epoxy. (f-h) Individual GQD structures and (i) Reactive amines on 4N and 6N-GQDs.

simulate tension in all the models [21–23]. Tensile simulations were run up to 10 % strain to focus on elastic modulus (E) and yield strength (σ_y). Fig. 1 outlines the modeling workflow; simulation details are given in the supplemental document.

3. Results

We synthesized four different nanocomposites with five different replicates, covering neat epoxy, pristine GQD-epoxy, 4N-GQD-epoxy, and 6N-GQD-epoxy (see Fig. 2 for abbreviations). Tension simulations were performed on these structures in the x, y, and z orientations—a total of 60 MD tensile tests (Fig. 2). The resulting crosslink densities and mass densities are within the range of experimental and MD results [24]. The initial GQD orientation was random for all the systems. The orientation of the GQDs with respect to the tensile load changed during deformation, this change was on average ~5° for all the GQD systems, which can be compared to in-situ small angle X-ray scattering (SAXS) experiments.

Table 1
MD predicted physical and mechanical properties and corresponding literature values. E is stiffness, and σ_y is yield strength.

Material	Crosslink density (%)	Density (g/cm^3)		E (GPa)	σ_y (MPa)	Free volume (%)		%
		IFF-R	ReaxFF			0 % strain	10 % strain	Change
Neat epoxy	82 ± 4	1.19 ± 0.01	1.23 ± 0.01	2.94 ± 0.95	109.4 ± 23.9	2.41 ± 0.30	2.89 ± 0.39	20
GQD-epoxy	87 ± 2	1.20 ± 0.01	1.23 ± 0.01	2.65 ± 0.74	103.4 ± 23.6	2.48 ± 0.07	2.91 ± 0.18	17
4N-GQD-epoxy	85 ± 3	1.15 ± 0.01	1.23 ± 0.01	2.96 ± 0.99	126.2 ± 30.7	2.49 ± 0.14	2.85 ± 0.30	15
6N-GQD-epoxy	84 ± 3	1.15 ± 0.01	1.24 ± 0.01	3.11 ± 0.67	127.6 ± 20.0	2.40 ± 0.29	3.04 ± 0.34	27
Experiments (epoxy)[25–27]	DoC = 1.00*	1.19–1.20		1.6–3.3	36–90			

* Experimental measurement is Degree of cure (DoC).

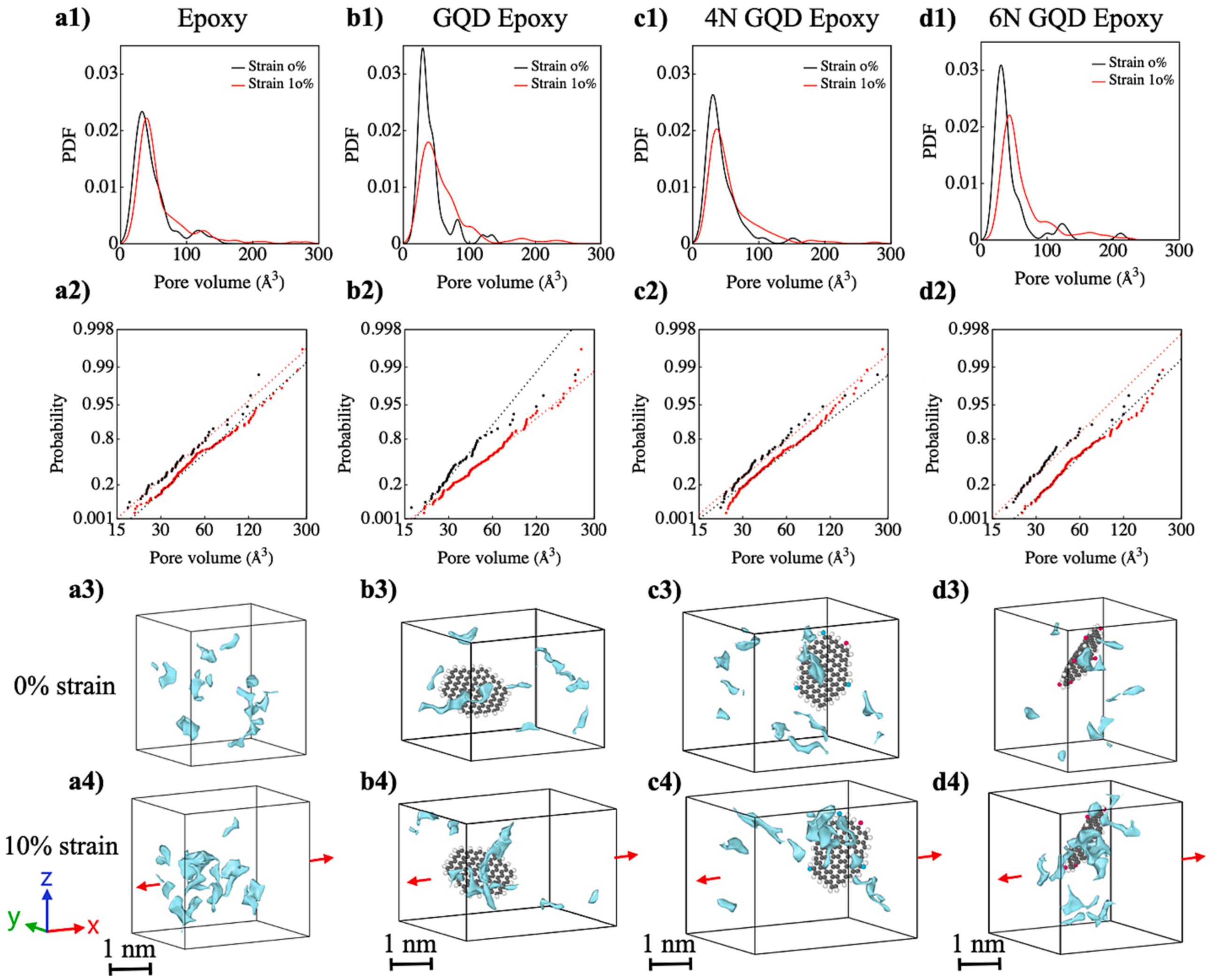

Fig. 3. Free volume analysis for the (a1-a4) neat-epoxy, (b1-b4) pristine GQD-epoxy, (c1-c4) 4N-GQD-epoxy, and (d1-d4) 6N-GQD-epoxy. (a1-d1) show the probability density function (PDF) of the voids for the four systems. (a2-d2) show the Fréchet distribution of ten largest voids. (a3- d3) illustrate locations of top ten voids and GQD in the simulation box at 0 % strain in a representative model. (a4- d4) illustrate the same information but at 10 % strain.

Our MD predicted E = 2.94–3.11 GPa and σ_y = 109–128 are consistent with the previous MD studies E = 4.3 ± 1.5 GPa and σ_y = 121 ± 36 MPa [18,21,24,28]. The addition of GQDs changed the mechanical properties. The addition of single layer functionalized 6N-GQD increased the average yield strength (σ_y) by 17 % from 109.4 MPa to 127.6 MPa. The increase in the number of amine groups from 4 to 6 increased both average stiffness E and σ_y, which shows the strong dependence of molecular structure and properties on the surface chemistry of the GQDs (Table 1). The effective load transfer at the edge covalent bonds due to amine functional groups was not present for the pristine GQD, which decreased the σ_y by 6 % and E by 10 %. Without covalent bonds at the edges, the pristine GQD interrupts the continuous amorphous network and lowers E. On the other hand, the addition of 6N-GQD increased E by 6 % and 4N-GQD by 2 %.

At the smallest scale, free volume affects the mechanical behavior. The average initial free volume for all the four systems was 2.41–2.49 % and increased with the strain (Table 1). The largest increase of 27 % was observed for the 6N-GQD system. The other nanocomposites showed an increase of 15–20 % (Table 1). We also explored the size of the voids, which showed that the addition of two extra functional groups to 4N-GQD enhanced the load transfer and created a larger change in free volume (Fig. 3 c1 vs. d1 and c2 vs. d2). Moreover, the free volume had opportunities to grow near the GQDs' basal plane as there are no covalent bonding sites on this plane (Fig. 3 b3-d3 vs. b4-d4).

4. Conclusion

We performed the first reactive MD simulations to virtually synthesize and mechanically test GQD-epoxy nanocomposites with three different GQDs—pristine GQD, 4N-GQD, and 6N-GQD. Sixty MD tension simulations were executed, from which the following conclusions can be drawn:

1. The functionalized GQDs increased the epoxy σy by 15–17 % for 4N-/6N-GQD-epoxy. Introducing amine groups to the GQDs' edges created covalent bonds with the epoxy matrix, which allowed the highest load transfer to the GQDs.
2. Lack of covalent bonds for the pristine GQD reduced the σy by 6 %. This creates opportunities to control plastic void growth at nanoscale to promote toughening in stiff thermosets.
3. The functionalized 6N-GQDs increased the epoxy stiffness by 6 %. Whereas the pristine GQDs reduced the stiffness by 10 %. Note that the pristine GQD can be seen as a defect that reduces both E and σy.
4. The change in free volume with the applied 10 % strain was the highest for the 6N-GQD-epoxy at 27 % compared to others at 15–20 %. These differences in free volume could cause different deformation behavior at higher strains by changing the nanovoid nucleation and growth.

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CRediT authorship contribution statement

Özgür Keleş: Conceptualization; Methodology; Formal analysis; Investigation; Resources; Writing - Review & Editing; Supervision; Project administration; Funding acquisition. **Prathamesh P. Deshpande:** Conceptualization; Methodology; Software; Validation; Formal analysis; Investigation; Resources; Data Curation; Writing - Original Draft; Writing - Review & Editing; Visualization.

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.

Data availability

Data will be made available on request.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.matlet.2024.136206.

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