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Determination of elastic constants of functionalized graphene-based epoxy nanocomposites: A molecular modeling and MD simulation study

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Abstract

The effect of carboxyl ($-\text{COOH}$) functionalized graphene (FG) on the mechanical properties of its epoxy-based nanocomposites has been investigated by Molecular Dynamics (MD) simulations. Simulations cells of nanocomposites with varying wt% of FG (1, 2 & 3 wt%) were constructed using Material Studio 6.0. Obtained MD simulation results show improved mechanical properties such as elastic modulus, bulk modulus, shear modulus, and the Poisson ratio of the FG/epoxy nanocomposites than that of pure epoxy. Moreover, the computational results of nanocomposites have also been validated well with existing experimental data. Therefore, the current MD simulation shows a decent computational sign for the existing experimental and simulation outcomes on mechanical properties of FG/epoxy nanocomposites.

Keywords: Mechanical properties; functionalized graphene; Cross-linked epoxy resin; Molecular Dynamics (MD) simulation.

1. Introduction

Graphene is a new two-dimensional (2-D) material, which was discovered in 2004. Due to its excellent mechanical, electrical, and thermal properties concerned wonderful interests from several engineering fields [1]–[4]. In recent times, functionalized graphene and its derivatives are used as a reinforced filler to improve the mechanical properties of polymer nanocomposites followed as potentially durable, tough, and lightweight materials [5]–[7].

Graphene is an allotrope of carbon one atom thick consisting of a single layer of carbon atom arranged in two dimensional (2-D) honeycomb lattice was discovered by Novoselov et al. [8]. In graphene, each atom is associated with its three closest sigma bond and put up one electron to a conduction band that expands above the entire sheet. Graphene is yet the centerpiece of many researchers doing efforts in the field of polymer nanocomposites [9]. Graphene can be manufactured by the exfoliation of graphite as a single layer, double layers, multilayers. The faith is increased in graphene outstanding has greater characteristics that high strength (1.0 TPa) [3] stiffness (0.7 TPa), thermal conductivity $3500 \text{ Wm}^{-1}\text{K}^{-1}$ and surface area ($2630 \text{ m}^2/\text{g}$) [10], [11], optical transmittance (97.7%) [12], electrical conductivity the recent density of 108 A/cm^2 and able to carrying densities of electrical higher than copper [13]. Researchers belong to the field of polymer composites that preferred graphene as a reinforcing element due to its outstanding mechanical and thermal properties [14].

Epoxies are also known as thermosetting polymers consist of 3D cross-linked structures. Epoxies with 3D cross-linked structures show enhanced properties to make the materials more attractive for various applications such as electronic packaging, adhesives, coatings,

composite materials, etc. Amongst various researchers' characteristics associated with polymers, limited efforts were made to study the cross-linking process and structure-property association of cross-linked polymers and their composites. In this paper, cross-linked structures are found by the reaction amongst LY556 epoxy resins and HY951 curing agents (hardeners). To accomplish 3D cross-linked structures, one of the reactants from the LY556 resin or HY951 hardener can be multifunctional. The cross-linked polymers have permanent covalent bonds and cannot be re-shaped and re-melted. Various investigators considered the epoxy polymers caused from EPON 862 resin cross-linked with triethylenetetramine (TETA) [15], [16] curing agents, and diethyl toluene diamine (DETDA) [17]–[20]. Cross-linking of DGEBA resin with methylene glycol di-p-aminobenzoate (TMAB) [21], isophorone diamine (IPD) [22], diamine [23], diamino diphenyl sulfone (DDS) [24], tri DETDA [25], (poly-oxy propylene) (POP) diamines [26] and methylene di-aniline (MDA) [27] were replicated studied by researchers. For instant, Tsige and Stevens [28] examined the effects of cross-linking functionality and interfacial bond density on the crack behavior of extremely cross-linked polymer networks. Hölck et al. [29] calculated the mechanical performance of the nanocomposite obtained by cross-linking amongst phenol novolac epoxy resin and bisphenol-A hardener. They have examined the interfacial properties of cross-linking of epoxy phenol novolac (EPN) and SiO₂ layers nanocomposites using MD. Also, various researchers examined the effect of Molecular dynamics (MD) simulations on the performance of cross-linked epoxy nanocomposites reinforced with SiC [15], Al₂O₃ [15] nanoparticles, and carbon nanotubes (CNT) [30], [31]. Further several studies associated with MD simulations and the modeling of cross-linked nanocomposites had been found in the literature [32]–[34].

Liang et al. [7] investigated the mechanical properties of graphene oxide (GO)/ poly (vinyl alcohol) (PVA) nanocomposites fabricated using a water solution processing method. They found that Young's modulus and tensile strength of nanocomposites increased by 62% and 72%, respectively, for low concentrations GO (0.7 wt%). Likewise, Qi et al. [35] fabricated liquid crystalline epoxy grafted GO infused epoxy composites. Results showed that the reinforcement of 1.5 wt% of fillers enhance the tensile strength of composites by 48% (from 55.43 to 80.85 MPa) compared to pure epoxy.

Now in days, molecular modeling and simulation of materials is an effective method to solve real-world problems at an optimized cost and its offers to explore the research up to a certain extent. Nayebi et al. [36] studied the mechanical properties of graphene/ polythiophene (PT) composites by MD simulations. Computed Young's modulus of graphene/PT composites was 99.6 GPa, which is higher than the calculated value of pure PT, i.e. 1.29 GPa, as well as the experimental value of 1.5 GPa. In another research, Lee et al. [37] examined the mechanical properties of FG reinforced epoxy nanocomposites based on their interaction energy using MD simulation. Results indicated that graphene functionalized with both $-\text{COOH}$ and $-\text{NH}_2$ functional groups improved the tensile strength, modulus, and toughness of nanocomposites. Lin et al. [38] examined that the Young's and shear moduli increased as graphene weight fraction rises and decreased as the temperature rises of graphene/PMMA nanocomposite with the help of MD simulations. Shen et al. [3] examined the mechanical properties of the nanocomposites at room temperature. And, Young's modulus of the epoxy was increased from 2 GPa to 3.1 GPa. Yu [39] examined Young's modulus of AG/epoxy nanocomposites through C-N

covalent bond was improved by 4.563 GPa, which is 51% higher compared with pure epoxy.

This paper examined the effect of –COOH-FG on the mechanical properties of FG reinforced cross-linked epoxy resin nanocomposites. Key investigation parameters such as (E, K, G, and ν) have been measured for three different wt% of –COOH-FG/ epoxy nanocomposites. MD simulation results were compared with the investigational results as well as in good agreement with the experimental work. Also, there is no analogous study on molecular simulation of LY556 epoxy resin cross-linked with DETA curing agent to estimate the mechanical properties of FG/epoxy nanocomposites with different wt% of graphene using MD simulation methods.

2. MD simulation section

2.1. Simulation Cross-linking Process between the DGEBA and DETA

Chemical structures of DGEBA and DETA before the cross-linking are of DGEBA LY556 epoxy resin ($C_{18}H_{21}ClO_3$) and DETA curing agent ($C_6H_{18}N_4$) represents in Figure 1. According to Figure 1(a), DGEBA consists of the bi-functional reactant by two epoxide groups at both ends, whereas Figure 1 (b) shows the DETA consists of five reactive sites with primary as well as secondary amine groups and hence is a multifunctional (fivefold-functional) reactant. Due to this, each DETA molecule can be reacted with five DGEBA molecules also capable to associate with another DETA molecule by its second epoxide head. Hence, DGEBA and DETA can produce 3D cross-linked epoxy polymers.

Figure 1. Molecular structures (a) LY556 epoxy resin (b) DETA before cross linking.

In LY556 epoxy resin, the C–O bond of each epoxide group is improved to form a reactive $-\text{CH}_2$ site represent in Figure 2, thus it can be cross-linked with a curing agent. Molecules of LY556 epoxy resin contain two epoxide groups at both ends which react with the hydrogen atoms present in amine groups of the HY951 curing agent. Additionally, the resulting resin molecule is again associated with the epoxy molecules at the site of HN and NH_2 groups' also one HY951 molecule is associated with another epoxide group. In conclusion, crosslinking between the LY556 epoxy resin and the HY951 curing agent has been established. The LY556 epoxy resin and HY951 curing agent molecules generate more crosslinks by keeping the reaction continuous. The motion of crosslinking's are in all directions and produced a network of macromolecules [40], [41].

Figure 2. Conversion of epoxide group to a reactive one through breaking the C–O bond.

2.2. Molecular modeling of cross-linked epoxy resin and carboxyl ($-\text{COOH}$) functionalized graphene

LY556 epoxy resin is used as a thermoset polymer matrix which has many epoxide groups for each molecule displays outstanding high elastic modulus, thermal conductivity, and corrosion resistance. Due to these exceptional properties, LY556 epoxy resin as a polymer matrix was used to construct polymer nanocomposites in different engineering areas. Figure 3(a) represented the molecular model of LY556. Hydrogen atoms present in the amine (-NH_2) groups of the curing agent (di-ethylene toluene di-amine –DETDA) react with the epoxide groups of epoxy resin molecules (Figure 3 (b)). Further, result cured resin molecules (Figure 3 (c)) react with the epoxy molecule at the site of HN and NH_2 and one curing agent molecule reacts at the site of another epoxide group. Hence, the cross-linking was established between the curing agent and epoxy resin represents in Figure 3(d). Finally, the effect remains, produces more cross-links motions in all directions between the curing agent and epoxy resin [41], [42]. All the constructed cells were relaxed through energy minimization processes using MD simulations package Material Studio 6.0. Graphene was functionalized with carboxyl groups, which are randomly attached to the carbon atoms of graphene sheet, as shown in Figure 4 (b).

Figure 3. Molecular structure of (a) LY556 epoxy resin (b) curing agent (TETA) (c) cured epoxy resin and (d) cross-linked LY556 epoxy resin.

Figure 4. Molecular model of pristine graphene (a), and -COOH functionalized graphene (b).

2.2. Simulation models

In the present work mechanical properties of FG/epoxy nanocomposites are predicted by MD simulations. After, equilibration process a model of FG/epoxy nanocomposite is represented in Figure 5, containing an amorphous cell-sized $4.48 \times 4.48 \times 4.48 \text{ nm}^3$, with a low density of 0.5 g/cc has been created at room temperature under the periodic boundary conditions. Energy minimization of MD simulations has been done to achieve the stable structure of a model, subsequently, the potential, lattice parameters, and non-bond energy are set. Later, step by step process of MD simulation has been completed with a time of 1 fs and 1 atm at 298 K, to obtain a real density and balance the system. After minimization, the system has been subjected to 270 ps at 298 K and 1 atm, to provide suitable kinetic energy to attain degrees of cross-linking, and a cut-off value of $5 \text{ \AA}$ has been adopted in our scheme to avoid highly strained structures and increased the chance of curing sites to fall within the reaction cut-off distance. Hence, new covalent bonds are formed and the cross-linking density is calculated. The above steps are replicate till no new covalent bonds are formed by the assumed cut-off distance ($5 \text{ \AA}$). At last, the final cross-linked models are slowly cooled at room temperature to get the elastic moduli we functional a strain of 0.005, and the thickness of the graphene sheet is assumed to be $3.4 \text{ \AA}$.

In this paper, the epoxy resin as LY556 (DGEBA) cross-linked with a curing agent as (DETDA) has been used as a polymer matrix. A single-layer graphene sheet with 164 carbon atoms was selected as a nanofiller in the nanocomposites. Chemical functionalization has been carried out to obtain a strong adhesive interface and good dispersion amongst the graphene and polymer chain. Many problems occur when

graphene was used as a reinforcing nanofiller in epoxy nanocomposites. To overcome these problems of dispersion as well as an agglomeration of graphene in polymer composites, a chemical covalent bond technique was used to maintain the stable bonds between FG and epoxy chains. Figure 6 represents the polymer structure of LY556 epoxy resin cross-linked with a curing agent (DETDA) containing 99 epoxy chains. Figures 7 (a-c) show the simulation cells of epoxy nanocomposites reinforced by three different wt% of -COOH-FG .

Figure 5: Molecular model of nanocomposite consists of cross-linked LY556 epoxy resin with -COOH-FG as filler.

Figure 6. Molecular model of LY556 epoxy resin as a matrix.

Figure 7. Molecular model of nanocomposites consists of –COOH-FG/ LY556 epoxy resin (a) 1 wt% (b) 2 wt% (c) 3 wt%.

2.3. Forcefield and simulation method

Polymer consistent force-field (*Pcff30*) forcefield was used throughout this research.

Pcff30 is the newest MD simulation technique used to adjust the *Pcff* computational

model. *Pcff30* has been used in the entire dynamic direction and many molecules as an *ab initio* force-field. *Ab initio* forcefield is used to determine the properties of many molecules like polymers, most repeated organics, and minor inorganic molecules [43], [44]. *Pcff30* forcefield contains three different classes of energy terms as cross-terms, the bonded energy terms, and nonbonded energy terms. Covalent bond stretching, torsion angle rotation energy, bond angle bending of the polymer chain represents the bonded energy terms. While, cross-terms and nonbonded energy terms are made of Coulombic electrostatic and the van der Waals force, correspondingly here the use of Lennard-Jones potential equation to obtained van der Wall interaction and the various functional forms in *Pcff30* force field has been discussed by H. Sun [45], and are as follows in Eq. 1:

$$E_{\text{total}} = E_{\text{valence}} + E_{\text{cross-term}} + E_{\text{non-bond}} \quad (1)$$

The valence energy term consisted of the covalent bond-stretching energy, E_{bond} ; the bond-angle bending energy, E_{angle} ; the torsion-angle rotation energy of the polymer chain, E_{torsion} ; and the out-of-plane energy, E_{oop} , as discussed in Eq. 2.

$$E_{\text{valence}} = E_{\text{bond}} + E_{\text{angle}} + E_{\text{torsion}} + E_{\text{oop}} \quad (2)$$

$$\begin{aligned} E_{\text{valence}} = & \sum_b [K_2(b - b_0)^2 + K_3(b - b_0)^3 + K_4(b - b_0)^4] \\ & + \sum_b [H_2(\theta - \theta_0)^2 + H_3(\theta - \theta_0)^3 + H_4(\theta - \theta_0)^4] \\ & + \sum_{\emptyset} \{V_1[1 - \cos(\emptyset - \emptyset_1^0)] + V_2[1 - \cos(2\emptyset - \emptyset_2^0)] + V_3[1 - \cos(3\emptyset - \emptyset_3^0)]\} \\ & + \sum_x K_x x^2 \end{aligned}$$

The terms for cross-interactions included the dynamic variations among the bond stretching interactions between two bonds, $E_{\text{bond-bond}}$; bond-bond interactions between two valence angles associated with a common vertex atom, $E_{\text{angle-angle}}$; stretch bond interactions, between a two-bond angle and one of its bonds, $E_{\text{bond-angle}}$; stretch-torsion interactions between a dihedral angle and one its middle bond, $E_{\text{middle-bond-torsion}}$; stretch-torsion interactions between a dihedral angle and one of its end bonds, $E_{\text{end-bond-torsion}}$; bend torsion interactions between a dihedral angle and one of its valence angles, $E_{\text{angle-torsion}}$; bend torsion interactions between a dihedral angle and its two valence angles, $E_{\text{angle-angle-torsion}}$, as discussed in Eq. 3.

$$E_{\text{cross-term}} = E_{\text{bond-bond}} + E_{\text{angle-angle}} + E_{\text{bond-angle}} + E_{\text{middle-bond-torsion}} + E_{\text{end-bond-torsion}} + E_{\text{angle-torsion}} + E_{\text{angle-angle-torsion}} \quad (3)$$

$$\begin{aligned} E_{\text{cross-term}} = & \sum_b \sum_{b'} F_{bb'} (b - b_0)(b' - b'_0) \\ & + \sum_{\theta} \sum_{\theta'} F_{\theta\theta'} (\theta - \theta_0)(\theta' - \theta'_0) \\ & + \sum_b \sum_{\theta} F_{b\theta} (b - b_0)(\theta - \theta_0) \\ & + \sum_b \sum_{\phi} F_{b\phi} (b - b_0)[F_1 \cos \phi + F_2 \cos 2\phi + F_3 \cos 3\phi] \\ & + \sum_{b'} \sum_{\phi} F_{b'\phi} (b' - b'_0)[V_1 \cos \phi + V_2 \cos 2\phi + V_3 \cos 3\phi] \\ & + \sum_{\theta} \sum_{\phi} F_{\theta\phi} (\theta - \theta_0)[V_1 \cos \phi + V_2 \cos 2\phi + V_3 \cos 3\phi] \\ & + \sum_{\phi} \sum_{\theta} \sum_{\theta'} K_{\phi\theta\theta'} \cos \phi (\theta - \theta_0) (\theta' - \theta'_0) \end{aligned}$$

The non-bond energy terms represent the Coulomb electrostatic force, E_{Columb} ; and the vdW force, E_{vdW} , as discussed in Eq. 4-5.

$$E_{\text{non-bond}} = E_{\text{Columb}} + E_{\text{vdW}} \quad (4)$$

$$E_{\text{non-bonded}} = \sum_{i>j} \frac{q_i q_j}{\epsilon r_{ij}} + \sum_{i>j} \left[\left(\frac{A_{ij}}{r_{ij}^9} \right) - \left(\frac{B_{ij}}{r_{ij}^6} \right) \right] \quad (5)$$

where q is the atomic charge, ϵ is the dielectric constant and r_{ij} is the distance between atom pairs.

‘ b ’ is the internal coordinates of the bond,

‘ b' ’ is the length of the other O–H bond,

‘ θ ’ is the bond angle,

‘ ϕ ’ is the torsion angle obtained by twisting the atoms about the bond axis,

x is the out of plane angle,

$K_i (i = 2 - 4)$, b_0 , $H (i = 2 - 4)_i$, θ_0 , $V_i (= 1 - 3)$, θ'_0 , $\phi_i^0 (= 1 - 3)$, $F_{bb'}$, $F_{\theta\theta'}$, $F_{b\theta}$, $F_{b\phi}$, $F_{b'\phi}$, $F_{\theta\phi}$, $K_{\phi\theta\theta'}$, A_{ij} , B_{ij} are fitted from quantum mechanics calculations and are implemented into the Discover module of Materials Studio.

Firstly, geometry optimization was done at the maximal displacement of 0.005 Å, atomic force 0.05 eV, the total energy 1×10^{-6} eV/atom, stress 0.005 GPa, and cut-off energy 270.0 eV. Furthermore, the amorphous cell was constructed at room temperature with the help of a module tool and parameters such as an initial density of 0.5 g/cc. Here, the –COOH-FG with wt% of 1, 2, and 3% and the number of loading is 1 consist LY556 epoxy resin with wt% (99, 98, 97 %) and the number of loading are 111, 55, 37. In all simulations, the atom is constructed with the help of MD simulation method to examine the elastic properties of nanocomposites by assuming the cut-off distance (5 Å). Medium-

range alterations are also functionalized on the cut-off distance to remove the nonbonded interactions hence, avoids the breaks produced by direct cut-offs.

2.4. Methodology to calculate mechanical properties

There are three main methods to evaluate the mechanical properties of nanocomposites by MD simulations, fluctuation formula [46], dynamics (constant-stress molecular dynamics), and static (constant-strain minimization) [47]. In the present work, the static method was used to calculate the mechanical properties of –COOH-FG based cross-linked epoxy systems. Stress-strain behavior for linear elastic materials can be described by Hooke's law (Eq. 6):

$$\sigma_i = C_{ij} \varepsilon_j \quad (6)$$

Where, $i, j=1, 2, 3$. σ_i and ε_j are the 6-dimensional stress-strain vectors, and C_{ij} is the 6×6 stiffness matrix. The strain amplitude was set to 0.005 to obtain the elastic constants. The stress components were calculated using the so-called viral expression (Eq. 7) [48].

$$\sigma_{ij} = -\frac{1}{V} \sum_k \left[m^k (u_i^k u_j^k) + \frac{1}{2} \sum_{i \neq j} (r_i^{kl}) f_j^{lk} \right] \quad (7)$$

Where V is the volume, m^k and u^k stand for the mass and velocity of the k^{th} particle, respectively, r^{kl} is the distance between k^{th} and l^{th} particles, and f^{lk} represents the force exerted on l^{th} particle by k^{th} particle.

The Lamé coefficients, λ and μ , can be calculated using any two of the following equations (8-13).

$$\lambda = \frac{1}{6} (C_{12} + C_{13} + C_{21} + C_{23} + C_{31} + C_{32}) \approx \frac{1}{3} (C_{12} + C_{23} + C_{13}) \quad (8)$$

$$\mu = \frac{1}{3} (C_{44} + C_{55} + C_{66}) \quad (9)$$

$$\lambda + 2\mu = \frac{1}{3}(C_{11} + C_{22} + C_{33}) \quad (10)$$

$$E = \frac{\mu(3\lambda + 2\mu)}{\lambda + \mu} \quad (11)$$

$$K = \lambda + \frac{2}{3}\mu \quad (12)$$

$$G = \mu \quad (13)$$

Where, K, E, and G are bulk, Young's, and shear moduli, respectively.

3. Results and discussion

The calculated mechanical properties of FG/LY556 cross-linked epoxy nanocomposites with graphene wt% (1, 2, 3 wt%) as illustrated in Table 5. Table 1 represents the elastic stiffness matrix of LY556 cross-linked epoxy which is obtained by the Forcite calculation available in the module tool of Material Studio software to calculate its mechanical properties. –COOH-FG acts as nano reinforcement while LY556 cross-linked epoxy resin act as a matrix in the nanocomposite's unit cell. Similarly, tables 2, 3 & 4 elucidate the elastic stiffness matrix of nanocomposites for 1, 2, and 3 wt% of –COOH-FG, respectively.

Table 1. Elastic stiffness matrix of LY556 cross-linked epoxy resin

C _{ij}	1	2	3	4	5	6
1	2.8591	31173	1.7135	0.4975	1.4771	1.6744
2	3.1173	11.3661	-2.0953	1.0571	0.4121	-2.6205
3	1.7135	-2.0953	-1.5148	-0.3648	-0.1665	0.9557
4	0.4975	1.0571	-0.3648	0.6777	0.2761	0.2752
5	1.4771	0.4121	-0.1665	0.2761	0.5612	-1.7748

6	1.6744	-2.6205	0.9557	0.2752	-1.7748	4.0594
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Table 2. Elastic stiffness matrix of 1 wt% –COOH-FG reinforced nanocomposites

C_{ij}	1	2	3	4	5	6
1	24.1300	9.2676	8.4630	-4.4538	3.4157	-1.1150
2	9.2676	22.9101	2.6848	0.9472	-0.0022	-1.3869
3	8.4630	2.6848	18.3195	0.7686	3.8437	-2.5435
4	-4.4538	0.9472	0.7686	13.8569	1.4798	-0.3663
5	3.4157	-0.0022	3.8437	1.4798	7.3565	-1.0363
6	-1.1150	-1.3869	-2.5437	-0.3663	-1.0363	9.45669

Table 3. Elastic stiffness matrix of 2 wt% –COOH-FG reinforced nanocomposites

C_{ij}	1	2	3	4	5	6
1	31.2087	12.6570	12.8638	0.0776	-0.0847	-1.0409
2	12.6570	28.5437	9.5530	0.5156	-2.0786	2.0324
3	12.8638	9.5530	34.5381	-4.3773	-1.5950	-0.7354
4	0.0776	0.5156	-4.3773	7.5284	1.5574	-2.4535
5	-0.0847	-2.0786	-1.5950	1.5574	8.7474	2.5715
6	-1.0409	2.0324	-0.7354	-2.4535	2.5715	10.6710

Table 4. Elastic stiffness matrix of 3 wt% –COOH-FG reinforced nanocomposites

C_{ij}	1	2	3	4	5	6
1	24.9376	0.5042	8.6270	-1.2550	-0.9807	1.7105
2	0.5042	25.1693	7.4412	-1.1087	-1.4330	0.0528
3	8.6270	7.4412	33.5204	-0.2203	-0.3764	-3.9620
4	-1.2550	-1.1087	-0.2203	12.9265	-1.4070	-1.2227
5	-0.9807	-1.4330	-0.3764	-1.4070	7.4964	-2.8382
6	1.7105	0.0528	-3.9620	-1.2227	-2.8382	14.2738

As the wt% of the FG increases from 1 to 2, 2 to 3%, at a constant volume, then LY 556 epoxy system is increased with the functionalized graphene molecules increases. Also, simulation results prove that the functionalized graphene-containing LY 556 epoxy resin system shows enhance mechanical properties compared to the pure epoxy resin system. Though, the enhancements are going with the variations. The results illustrate that the functionalized graphene-containing LY 556 epoxy resin system with a 3% weight fraction has advanced elastic moduli compared with the others. This result is defined by a fact that additional functionalization in functionalized graphene LY 556 epoxy remains as combined particles. The results have a good arrangement with the experimental accomplishment by Lee et al. [37] estimated the improved mechanical properties of epoxy nanocomposites infused with graphene containing both $-NH_2$ and $-COOH$ functional groups. MD result indicated that the tensile modulus of above-mentioned nanocomposites increases from 3.1 GPa to 3.45 GPa as compared to $-COOH$ -FG reinforced nanocomposites. Sun et al. [49] noticed that Young's modulus of graphene/epoxy nanocomposites increases by 2.74 GPa with filler wt% of 0.88. Likewise, Rafiee et al. [50] examined the enhancement of elastic modulus is increased by increasing the functional groups with the help of the experiment and various results represented in Table 5.

Approximately, all the examined results for mechanical properties, such as Young's modulus, bulk modulus, the shear modulus is higher than the experimental results as well as compared to simulation results because the simulation systems have no imperfections and is an ideal situation whereas numerous types of imperfections are present in physical models that result in the compact calculated properties. As represents in Table 5, the

examined value of the elastic modulus is higher than the experimental value. Hence, by increasing the number of atoms in the cell, improved material properties are found.

Table 5. Mechanical properties of –COOH-FG/ epoxy nanocomposites at room temperature

Materials	wt% of fillers	Young's modulus of pure epoxy (GPa)	Nanocomposites				Method Adopted	Ref.
			Young's modulus (GPa)	Bulk modulus (GPa)	Shear modulus (GPa)	Poisson ratio		
Gr-COOH	1	3.24	3.55	–	–	–	Experiment	[37]
–COOH + –NH ₂ Graphene			3.66	–	–	–		
Gr-COOH			3.60	–	–	–		
Gr-COOH	1.2	–	4.55	–	–	–	MD	[39]
–COOH Graphene	0.88	2.74	4.68	–	–	–	MD	[49]
GS-sPMMA	–	3.8	4.7	0.36	1.4	0.36	MD	[51]
FGS-sPMMA	–	6.0	5.0	0.31	2.3	0.31		
f-GNPs	1.5	–	6.80	–	–	–	Experiment	[52]
–NH ₂ graphene	1	–	3.1	–	–	–	Experiment	[53]
Intercalated graphene	1	3.24	5.63	–	–	–	MD	[54]
Intercalated GO		3.16	6.36	–	–	–		
Graphene flakes		3.16	5.48	–	–	–		
GO/f-GO	0.1	–	3.6	–	–	–	Experiment	[55]
GNPs	1	–	2.8	–	–	–	MD	[56]
Sulfonic GO	1	–	2.36	–	–	–	Experiment	[57]
GO	1	1.66	2.25	5	11	–	MD	[58]
Diazonium-FG	0.8	–	3.20	–	–	–	Experiment	[59]
GO	0.5	–	1.70	–	–	–	Experiment	[60]
FGO	1	–	2.89	–	–	–	Experiment	[61]
Gr-COOH	1	–	9.3	–	4	0.5	MD	[62]
–COOH + –NH ₂	1	–	9.4	–	–	–		

Graphene								
GO	2	–	4.45	–	–	–	Experiment	[63]
–NH ₂ -f-Gr	1	–	3.55	–	–	–	Experiment	[64]
–COOH Graphene	0.1	2.85	3.74	–	–	–	Experiment	[65]
Pure epoxy	–	–	4.04	1.8823	1.7661	0.04	MD	Pres ent work
–COOH-FG/ epoxy nanocomposites	1	–	9.53	8.15	10.23	0.05		
	2	–	23.35	19.45	8.98	0.60		
	3	–	26.49	12.45	11.56	0.15		

4. Conclusions

Molecular modeling of –COOH-FG /epoxy nanocomposites has developed to determine the elastic constants such as Young's modulus, bulk modulus, shear modulus, and Poisson ratio. In this study, the MD simulation approach with *Pcff30* force-field has been effectively applied to simulate the cross-linked DGEBA (LY556 epoxy resin) with DETA curing agent, nanocomposites with different wt% of FG. The constant strain approach has been used to calculate the mechanical properties of nanocomposites. The MD results showed that the mechanical properties of nanocomposites significantly improve by adding –COOH-FG to cross-linked epoxy. The best results were obtained at 3.0 wt% of FG, which was in good agreement with experimental as well as related MD simulation work. The MD simulation showed more interaction energy amongst the graphene and surrounding matrix for higher wt% of graphene and –COOH functional groups. Therefore, –COOH-FG is used as a filler material to improve the elastic constants of the FG/epoxy nanocomposites. Comparing the simulation results with experimental and MD simulation data recognized that the current MD simulation shows a decent

computational sign for the existing experimental and simulation outcomes on mechanical properties of FG/epoxy nanocomposites.

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Conflict of interest

The authors declare no conflict of interest.

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Authors' contributions

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