INVESTIGATION OF MECHANICAL PROPERTIES OF GRAPHENE REINFORCED EPOXY NANOCOMPOSITE USING MOLECULAR DYNAMICS

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Abstract. Graphene is a two-dimensional hexagonal type of carbon allotropes in the form of a sheet. It is a one atom thick sheet of carbon atoms, which has extraordinary thermal, mechanical, electronic and electrical properties. In the present research, a molecular dynamic study has been done to investigate the mechanical properties of graphene reinforced epoxy nanocomposite. A single layer of graphene sheet has been randomly reinforced into the epoxy matrix at 5%, 10%, 15% and 20% weight percentages. A dense amorphous cell is created using the Forcite module of Material Studio software and simulation is performed. Young's modulus is predicted at varying strain rate from 0-1. Results have revealed that Young's modulus increases with increase in reinforcement quantity. Moreover, graphene reinforced epoxy nanocomposite exhibits better properties than CNT reinforced nanocomposites.
Keywords: atomistic model, epoxy, graphene, molecular dynamics, Young's modulus

1. Introduction

The nanocomposite is a multiphase solid material where one of the phases has one, two or three dimensions of less than 100 nanometers (nm). Nanocomposite materials have emerged as suitable alternatives to overcome limitations of microcomposites and monolithic while posing preparation challenges related to the control of elemental composition and stoichiometry in the nanocluster phase. These are reported to be the materials of the 21st century in the view of possessing design uniqueness and property combinations that are not found in conventional composites. The effectiveness of the nanoparticles is such that the amount of material added is normally only between 0.5 and 5% by weight.

Over the past decade, advanced material researchers had focused on the development of polymer based nanocomposites reinforced with well-defined nanostructured compounds, which are expected to provide high performance materials, with potential application in a wide range of technological areas such as defense, aerospace, automotive industries etc. The properties of materials may be enhanced by reinforcing with a different type of superior materials like carbon nanotubes (CNTs), Graphene (GR), nano rope, nanoclay and metal/polymer based nanoparticles. However, Graphene has attracted the significant attention of researchers of various areas and has been found to be a suitable reinforcing candidate due to its superior properties over CNT and other nanoparticles. Graphene reinforced polymer nanocomposites have attracted the attention of researchers and material scientists due to its superior properties over other reinforcement materials like CNTs etc. As per the literatures,

nearly 98% of CNTs are produced defective and having structural discontinuities which restrict the application of CNTs in reinforced nanocomposites. The defective CNTs may react with the base material due to which the desired properties may not be achieved. A certain advantage of GR such as high aspect ratio, non-functionality, better electronic and thermal conductivity, thermal stability over the CNTs makes it a potential reinforcement candidate for polymer based nanocomposites. Moreover, mechanical properties and gas barrier behavior appears as a highly promising additive for the improvement of the overall performance of the host polymeric component. In general, the physical properties of such mixed systems were found to depend on several parameters, among others on the characteristics of the dispersion of the GR layers and the nature of the interactions between GR and the polymeric matrix, the amount of wrinkling in the GR, the polymer architecture and the sample preparation procedure [1-3]. Graphene is also envisioned as the key ingredients of many futuristic applications. In particular, epoxy nanocomposites with improved properties (elastic modulus, tensile strength, and toughness) are obtained by reinforcing Graphene into epoxy matrix [4], which make the nanocomposites ideal for various applications viz. lightweight gasoline tanks, strong wind turbines, medical implants, sports equipment, etc. [5]. In addition to the improvement in mechanical properties, graphene reinforced nanocomposites often exhibit enhanced thermal properties and electrical properties as well [6]. Moreover, graphene based nanocomposites have unique applications in a broader range of industries. Thin-film capacitors for a computer chip, Solid polymer electrolytes for batteries, automotive and aircraft engine parts and fuel tanks etc.

Epoxy resins are the well-known class of thermosetting polymers which are widely used as adhesives, electronic encapsulating compounds, coating materials and the organic phase of composite materials due to their high mechanical strength, high chemical corrosion and erosion resistance, excellent electrical insulation. DGEBA (Diglycidyl Ether of Bisphenol-A) categorizes as a thermosetting polymer which has excellent cross linking property and forms polymer chains which may have an irreversible network structure. In this context, various researches have been done highlighting the importance of polymer based nanocomposites and reinforcement of GR and carbon nanotubes (CNTs). Xia et al. [7] investigated the interfacial mechanical behavior of multilayered graphene-PMMA layered nanocomposites by performing pull-out simulations using MD. The results revealed two distinct failure mechanisms; namely, pull-out failure (failure along graphene-PMMA interface) and yielding failure (failure within the multilayered graphene). A one-step cross-linking of epoxy networks was performed by Yarovsky and Evans [8]. The cross linking was based on local proximity keeping the cutoff distance and reactivity orders of the various epoxy. Site pairing was done considering the cutoff distance of 6 Å and crosslinking were based on proximity and reactivity weights. It was observed that the adopted method was not precise enough to obtain a high percentage of curing compared to that obtained synthetically. The cross-linking mechanism was reported by Rottach et al. [9] stated two-stages cross-linking which consists of unstrained and uniaxial strained. Xia et al. [10] conducted coarse-grained molecular dynamics (MD) simulations of nano-indentation of PMMA polymer to study the variation of the elastic properties near the interface between the indenter and the substrate. Characterization of elastic properties was performed by Griebel et al. [11] on polymer-carbon nanotube composites by applying MD simulations, wherein polyethylene was reinforced with CNT. Zhao et al. [12] reported improvement in compressive fracture strength and plastic strain of the composite based on his study regarding the impact of CNTs on the mechanical properties of Magnesium based amorphous alloys. Microstructure characterization method was used by Wan and Chen [13] to examine changes in modulus improvement as a result of interfacial interactions between graphene oxide and the polymer matrix. Awasthi et al. [14] studied the amount of load transfer between a graphene sheet and polyethylene on a nano

scale by utilizing the method of MD simulations. The authors had concluded that the graphene sheets appeared to be adhered to polymer chains in a specific zone and the interphase layer remained unaffected. Shin et al. [15] adopted modelling approaches on epoxy nanocomposites to identify and permeate the interfacial behavior and interphase properties. A reduction in interfacial adhesion with an increase in crosslink conversion was observed between the matrix and the filler. Through MD simulation work of crosslink density on the molecular structure of the interface for the graphite fiber/epoxy matrix, Hadden et al. [16] proved that the effective surface thickness from the graphene sheet is insensitive to the variation of crosslinking. Li et al. [17] dealt with multilayer graphene for the investigation of the interfacial layer of cross-linked epoxy, focusing on the various orientation of the layers by MD simulations.

Dai and Mishnaevsky [18] studied the damage and fracture of graphene reinforced nanocomposites using 3D computational model. The damage mechanisms were studied considering the effect of the aspect ratio, shape, clustering, orientation and volume fraction of graphene platelets. It was observed that the Young modulus of the nanocomposites significantly influences by these parameters and increases with increasing aspect ratio, volume content, elastic properties of graphene/polymer interface layer, and decreasing the degree of intercalation. Roussou and Karatasos [19] employed a full atomistic molecular dynamics simulation and studied the melt dispersions of graphene nanosheets in a poly (ethylene glycol) (PEG) matrix at various temperature ranges. Two different polymer sizes were investigated and resultant mixtures were characterized after reinforcement of graphene in PEG oligomeric clusters. Sharma et al. [20] had used molecular dynamics simulation to study the mechanical and thermal properties of graphene–carbon nanotube-reinforced metal matrix composites. The authors had considered two different computational models viz. single layer graphene sheets–copper and carbon nanotube–copper composites at various temperature and volume fraction of the reinforcing materials. It was found that with an increase in volume fraction Young's modulus as well as the thermal conductivity of single layer graphene sheets–Cu composites increased at a faster rate than that for carbon nanotube–Cu composite. Keeping the volume fraction constant for carbon nanotube and graphene, it has been reported that Young's modulus of single layer graphene sheets–Cu composite was higher than carbon nanotube–Cu composite. Tensile behavior of graphene reinforced polymer nanocomposite was reported by Sun et al. [21]. The authors had used defective single layer graphene which contained single or double vacancies using molecular dynamics simulations. It has been concluded that the mechanical properties such as Young's modulus, ultimate strength and strain in both directions decrease with an increase in defects.

In the present study, molecular dynamics simulation has been employed to determine the mechanical properties of graphene reinforced epoxy nanocomposite. A fully atomistic model of epoxy has been built in Material Studio visualizer and curing has been done using hardener Diethyltoulenediamine (DETDA). Diglycidyl ether of bisphenol A (DGEBA) has been selected for matrix material. An amorphous cell has been created using a single layer of a graphene sheet by random reinforcement. Mechanical properties of epoxy nanocomposite have been determined with and without the reinforcement of graphene sheet.

2. Model and Method

In the present research, molecular dynamics simulation has been performed using Material Studio software. MD is the most detailed molecular simulation method [22] which computes the motions of individual molecules. Coupled Newton's equations of motion, which describe the positions and momenta, are solved for a large number of particles in an isolated cluster or in the bulk using periodic boundary conditions. The equations of motion for these particles which interact with each other via intra and inter-molecular potentials can be solved

accurately using the following numerical integration methods (a) common predictor-corrector and (b) Verlet method. MD efficiently evaluates different configurational properties and dynamic quantities which cannot generally be obtained by Monte Carlo simulations [23]. In the present research, a fully atomistic model has been built in the material Studio visualizer environment. A rigid triangular structure has been modeled (shown in Fig. 1) and densely packed in an amorphous cell which is a representative of the actual composite as reported by Dikshit and Engle [24] as shown in Fig. 2.
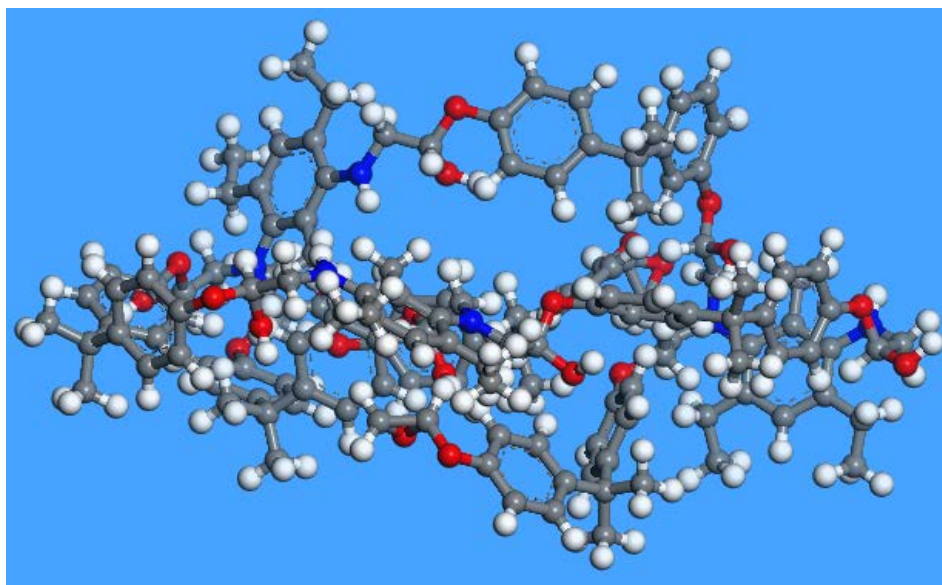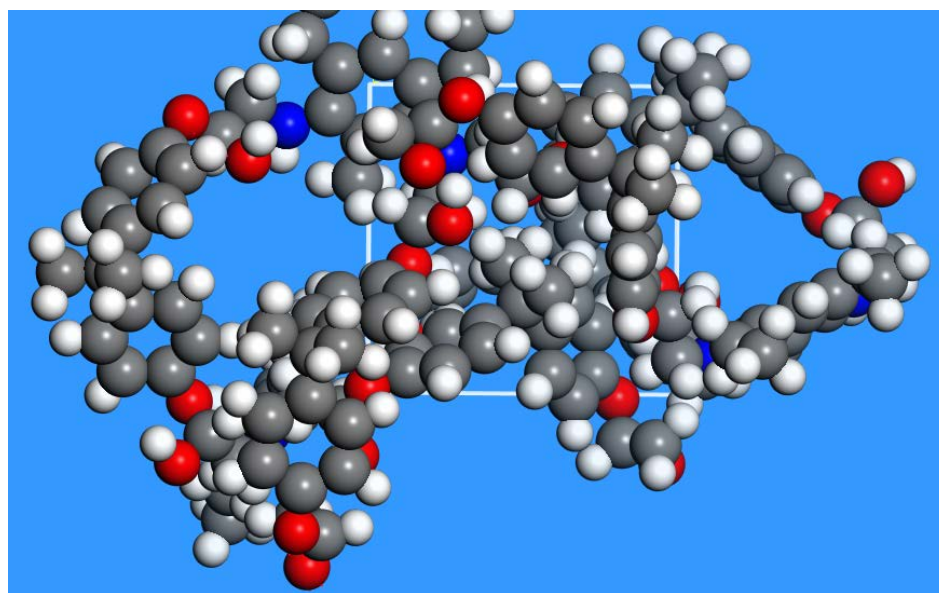

Fig. 1. Triangular model of cured DGEBA [24]

Fig. 2. Amorphous cell of the triangular model

In the course of building an amorphous cell the target density of cell was kept equivalent to the real density of the epoxy DGEBA i.e. 1.2 gm/cm^3. In densely packed amorphous cell 20 molecules of the triangular model have been used (Fig. 2). Energy minimization and geometric optimization have been employed to stabilize the structure. Dynamic stability has been done using the Forcite module employing NPT ensembles. Furthermore, annealing has been performed using the NVT ensemble to keep volume and density intact. The dynamic run has been done followed by energy minimization and

geometry optimization. The control parameters for Forcite Dynamics and Forcite Anneal Dynamics are depicted in Table 1 and Table 2 respectively.

Table 1. Control Parameter Employed for MD Simulation (Forcite Dynamics)

Force-field	COMPASS II
Temperature control	Berendsen
Pressure Control	Berendsen
Initial velocity	Random
Temperature	298 K
MD ensemble	NPT
Pressure	0.3 GPa
Time step	1 femtosecond (fs)
Duration of simulation	10 pico second (ps)
Periodic boundary condition	On
Number of steps	20000
Frame output every	1000 steps

Table 2. Control Parameter used for Forcite Anneal Dynamics

Anneal cycles	10
Initial Temperature	298 K
Mid-cycle temperature	500 K
Heating ramps per cycle	5
Dynamics step per ramp	100
Total number of step	10000
Geometry optimization after each cycle	yes

The simulation has been done at room temperature i.e. 25ºC (298 K) and external pressure was 0.3 GPa. Fig. 3 shows the temperature stability of the developed model with time. From Fig. 3 it can be seen that initially, the temperature of the model increases and rose to the room temperature. As the simulation proceeds, there is no change in the temperature profile which suggests that the model is dynamically stable. Using the control parameters as depicted in Table 1, the predicted density of the developed amorphous cell is 1.202 gm/cm^3 (shown in Fig. 4) which is very close to the actual density of the epoxy DGEBA at room temperature. Furthermore, the stability of the developed model has also confirmed the Forcite Dynamics energies trajectory as shown in Fig. 5.
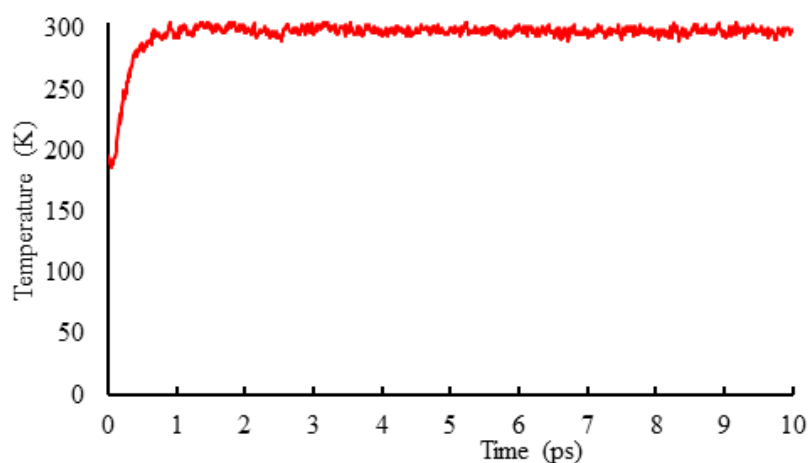

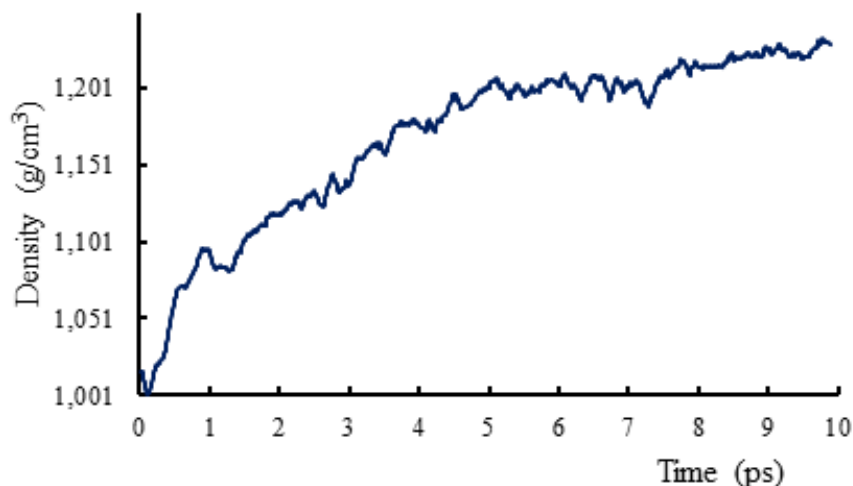**Fig. 3.** Simulated data for temperature (K)

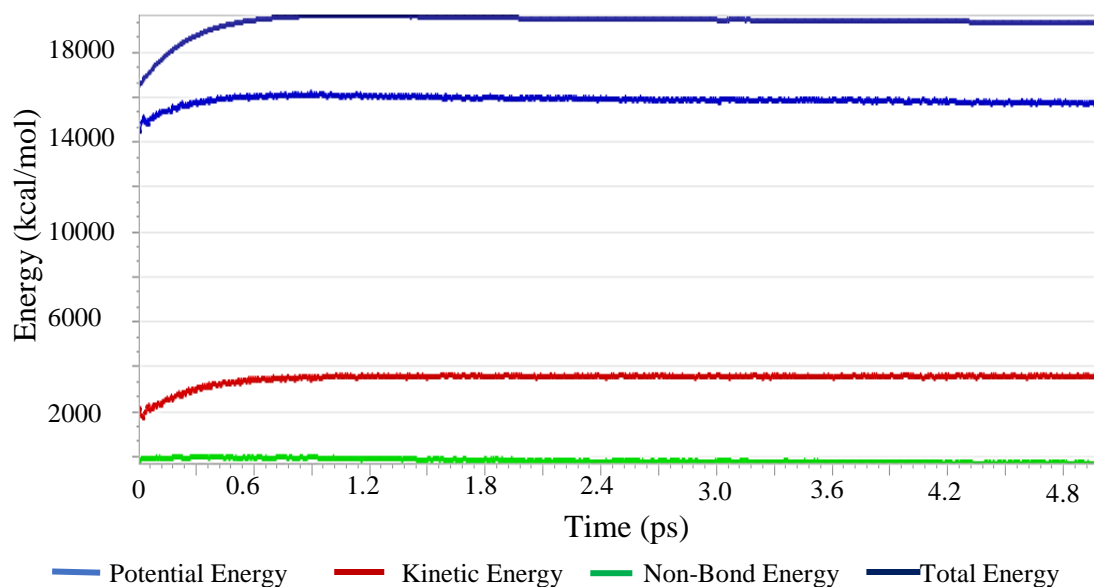**Fig. 4.** Simulation data for density (g/cm^3)

Fig. 5. Forcite energy diagram for the simulated amorphous cell of DGEBA

From Fig. 5, it is observed all the energies (potential energy, kinetic energy, non-bond energy and total energy) are constant as the simulation progresses. Lower the kinetic energy more stable is the model which also confirm the thermal stability of the model. The optimized structure is further used for creating graphene sheet reinforcement to obtain a graphene based nanocomposite. A single layer graphene sheet (5 repeat units and consisting of 72 atoms) has been randomly reinforced into the epoxy matrix shown in Fig. 6. In the present research, reinforcements have been done at a various weight percentage of graphene viz. 5%, 10%, 15% and 20%.

Similar simulation processes have been adopted using the control parameters depicted in Table 1 and Table 2. After ensuring the stability of the developed model, the model has been further processed for predicting mechanical property.
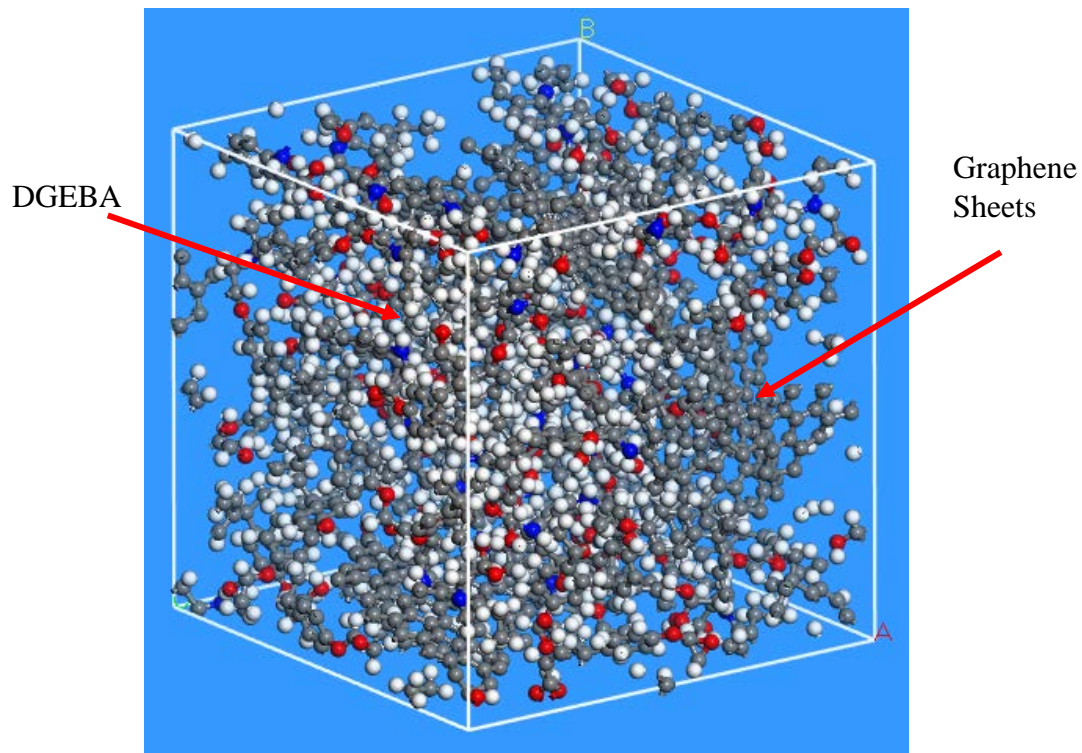
DGEBA

Graphene
Sheets

Fig. 6. Amorphous cell model for graphene reinforced epoxy

3. Results and Analysis

MD simulation has been employed on two amorphous cell models. One model consists of cured DGEBA and another model is obtained after reinforcement of a graphene sheet into the matrix of DGEBA. The simulation has been performed according to the discussions depicted in section 2. The mechanical properties have been obtained after the Forcite dynamic simulation with constant strain minimization. Simulations using COMPASS II force-field have been performed in the Forcite module. Simulations have been performed at room temperature (298 K) using the triangular model as described in section 2. Young's modulus has been predicted at 0%, 2%, 4%, 6%, 8%, and 10% of strains. Predicted Young's modulus of DGEBA without reinforcement at 0% strain is reported to be 2.429 GPa at 298 K and the corresponding Poisson ratio 0.42 [24]. The simulation has been done on the developed graphene reinforced epoxy nanocomposite at a different weight percentage of the graphene sheet. Stress vs. strain curves are plotted for each weight percentage (i.e. 5%, 10%, 15% and 20%) shown in Fig. 7.

The figure (Fig. 7) depicts the stress at various strain rates of DGEBA reinforced with a different weight percentage of graphene and the one without reinforcement. From Fig. 7 it can be seen that there is a significant improvement in the stress value of the epoxy with the increasing value of reinforcement. Superior property is obtained at 20% weight faction of graphene. However, nonlinearity has been observed in the stress vs. strain curve of graphene reinforced epoxy nanocomposite at 20% weight of graphene, this might be due to improper interphase or improper dispersion of large quantity of graphene.

The plot of Young's modulus against various strain rate at different weight percentages of graphene and without reinforcement is shown in Fig. 8. From Fig. 8, it can be observed that there is a substantial increase in Young's modulus with reinforcement at the same strain rate. Similarly, the maximum value of Young's modulus at 0% strain rate for the simulations involving reinforcement of graphene at a weight of 20% and 15% were found to be around 17.8 GPa and 12.4 GPa respectively and the values of those with 10% and 5% graphene were 8.45 GPa and 4.8 GPa respectively. It is also observed that the value of Young's modulus

decreases with increase in strain rate. Moreover, the obtained results of the graphene reinforced epoxy nanocomposite are compared to CNT reinforced epoxy nanocomposite as reported by Dikshit and Engle [24]. It has been found that graphene reinforced epoxy nanocomposite exhibits better mechanical properties when compared to CNT reinforced epoxy nanocomposite.
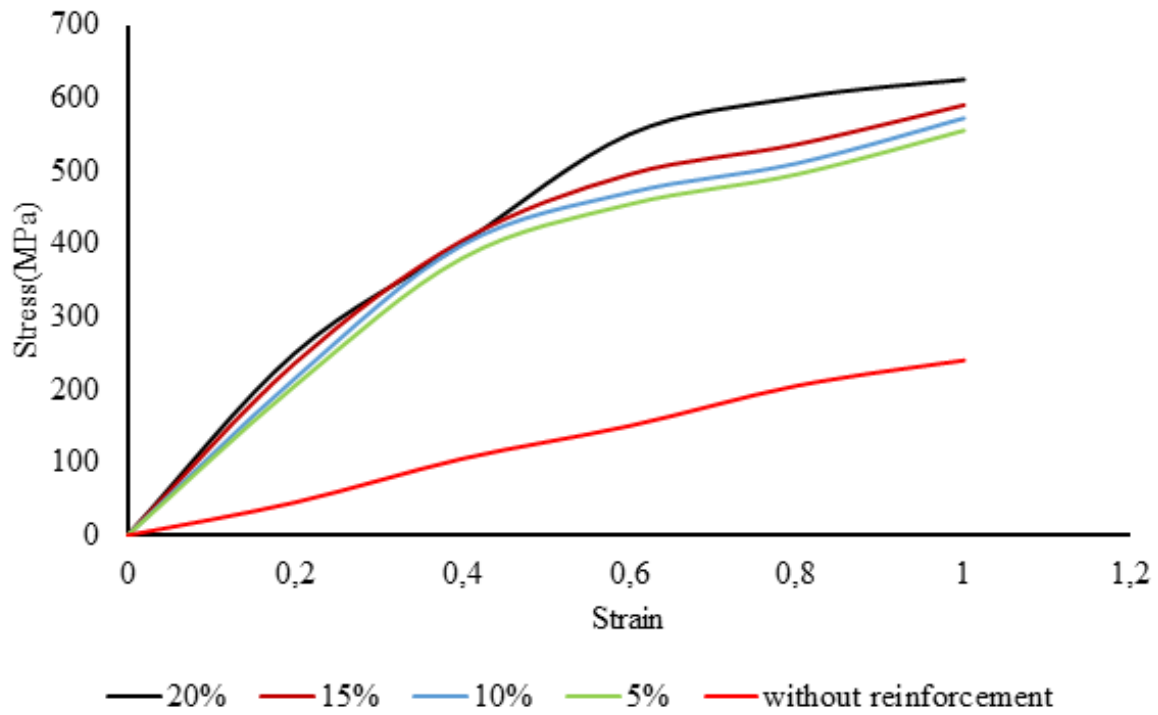

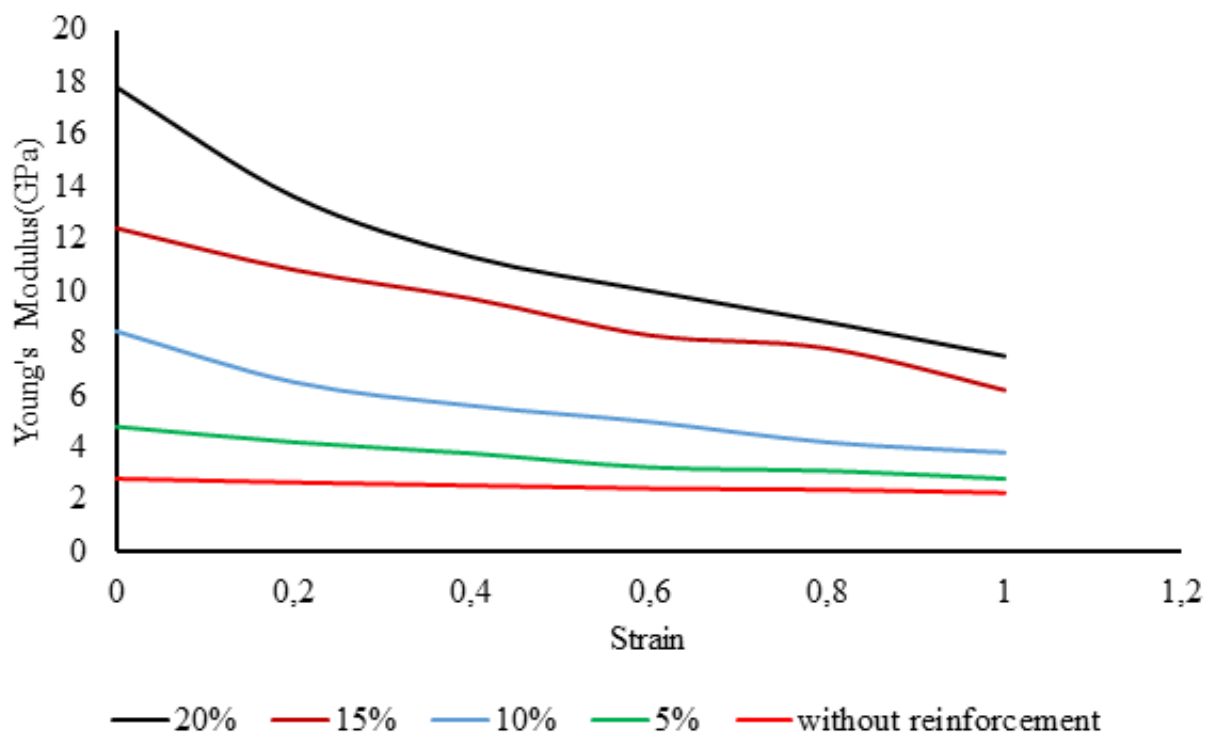**Fig. 7.** Stress v/s Strain at different weight percentage

Fig. 8. Young's Modulus v/s Strain at different weight percentage

4. Conclusions

Molecular Dynamics simulations have been employed to study the elastic properties of the epoxy DGEBA cured with DETDA, graphene reinforced epoxy/graphene nanocomposite. Two models of composites have been studied: (a) epoxy matrix with graphene reinforcement and (b) without graphene reinforcement. The following conclusions are drawn from the present research.

1. The predicted MD simulations results for epoxy DGEBA-DETDA indicate that the elastic modulus decreases consistently with the increase in strain. Elastic moduli of the epoxy DGEBA cured with DETDA decreases with the increasing strain levels.

2. The elastic modulus of the epoxy nanocomposite (with or without reinforcement) decrease with increase in strain levels (from 0.0 to 0.1). The MD simulation results clearly indicate that Young's modulus of the Graphene reinforced composites is superior to the DGEBA epoxy matrix.

3. At any given strain level graphene reinforced epoxy composite is 8 times stiffer than the pure epoxy matrix. Whereas in the case of DGEBA reinforced with CNT [24] it is found that the composite is 4 times stiffer than its pure form.

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