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INVESTIGATION OF MECHANICAL PROPERTIES OF CNT REINFORCED EPOXY NANOCOMPOSITE: A MOLECULAR DYNAMIC SIMULATIONS

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Abstract. In the present research, MD simulations have been employed to study the mechanical properties of epoxy DGEBA with and without reinforcement of CNT. A triangular cross link rigid structure has been created using Material Studio (MS) software. An amorphous cell has been created which is a reprensentative composite. All the simulations have been carried out using Forcite module of Material Studio. Mechanical properties with and without reinforcement of CNT have been obtained. It has been found that at room temperature, Young's modulus of DGEBA-DETDA composite is 2.429 GPa while after reinforcement of CNT, Young's modulus increased to 13.27 GPa. The MD simulation results indicate that the Young's modulus of the reinforced composites and the epoxy matrix decrease with increase in strain rate (from 0.0 to 0.1). MD simulation results show that at any given strain rate, CNT reinforced epoxy composite is 5 times stiffer than the pure epoxy matrix.

Keywords: carbon nanotube; DGEBA; epoxy; molecular dynamics.

1. Introduction

High performance composites were born for the needs of the extremely high performance of aircraft constructions during Cold war. Based upon their high performance properties, reduced cost manufacturing methods and higher level of confidence among the users, the use of composites has expanded greatly. Composites are now used in various fields like defense, sports, recreation market and medicals. Rockets and missiles experience the temperature of around 2000 – 3000 °C, when entering into the earth's atmosphere. Majority of metals cannot withstand such high temperature. However, composites can withstand a temperature of above 2000 °C. In addition, composites have significant advantages and applications over other materials like metal, ceramics etc. Composites have replaced metals in many applications.

Some properties of material can be improved by developing them as composite materials, namely: strength, stiffness, corrosion and wear resistance, fatigue life, weight, temperature dependent behavior, thermal insulation, thermal conductivity and acoustic insulation. In addition to above properties, composites have cost and weight advantages. Chemically cross-linked thermosetting polymer networks are pervasive in army applications including composite protective materials, nanocomposites, anticorrosive coatings, polymer membranes, laminate structures, and electronic devices. Epoxy is one of the most commonly used resins in the polymer matrix of fiber-reinforced composites, where it is typically cross-linked with amine curing agents to form a fiber-adhering network. Epoxy is also frequently

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used in adhesives, coatings, and paints. Moreover, they are intensively used in structural and specific composite applications because of their highly tunable thermo-mechanical properties that are unattainable with other thermoset resins [1]. Epoxies also offer high strength, low shrinkage, excellent adhesion to various substances, effective electrical insulations, chemical and solvent resistance, low cost and low toxicity.

In the present research Epoxy LY 556, chemical name Diglycidyl Ether of Bisphenol-A (DGEBA) has been used for epoxy matrix. DGEBA categorize itself as a thermosetting polymer with highly crossing linked polymer chains that form an irreversible network structure. As a result, this material is very strong due to tight linkage. Plenty of studies have been done in literatures to understand the cross-linking properties and mechanical properties of epoxies. Yarovsky and Evans [2] performed one-step cross-linking of small (~10 to 15 monomers) epoxy networks, based on local proximity, within a reaction cutoff distance and reactivity orders of the different epoxy. All site pairs were within the cutoff (6 Å) and cross-linked together according to proximity and reactivity weights. However, the method was not able to reach high percentages of curing comparable to that reached synthetically. Tack and Ford [3] built a set of pre-cured (cross-linked) oligomeric molecules of around 20 monomers each. These were densely packed about ~10 of monomers into a box to approximate larger and more highly cross-linked networks. Rottach et al. [4] performed two-stage (unstrained and uniaxial strained) cross-linking, followed by scission of various cross-links from the unstrained stage to measure the stress response and compare with a generalized independent network hypothesis. Varshney et al. [5] compared two different multi-step cross-linking algorithms (a) shortest pair of reactive sites and (b) all reactive pair sites for building epoxy networks cross-linking. Cross-links were formed by ramping up a harmonic bond potential in a 5-step process over time. It was suggested that equilibration and cross-linking could be repeated as necessary until the desired cross-linking density achieved.

Lin and Khare [6] employed simulated annealing technique with path-reversal Monte Carlo (MC) moves followed by restrained MD to optimize the sum of cross-link bond lengths in a one-step mixture polymerization of epoxy and epoxy-POSS-nanocomposite systems. These systems ranged in size from ~150 to 300 monomers with the stoichiometric ratio of DGEBA epoxy monomers to tetramethylammonium bromide (TMAB) cross-linkers of 2:1. Komarov et al. [7] applied four-stage algorithm for constructing highly cross-linked epoxy resins: (i) coarse-graining monomer units and randomly placing them onto a cubic lattice; (ii) cross-linking the monomer lattice using a combination of random cross-link selection, distance criteria trial-and-error attempts, and MC translation/rotation moves to relax the dynamically cross-linking CG system; (iii) reverse-mapping the cross-linked CG representation back into atomistic detail; and (iv) simulating the atomistic representation of the cross-linked system. The first two stages could be readily adapted to other monomer mixture preparation and cross-linking procedures while retaining the computational benefits of building a CG model and then back-mapping to atomistic detail.

A multiscale modeling approached was proposed by Shin et al. [8] to characterize the interfacial behavior and the interphase properties of epoxy nanocomposites. Molecular dynamics and molecular mechanics were used to study the interfacial characteristics between filler and matrix. The authors had reported that the interfacial adhesion between the filler and matrix reduced with increase in crosslink conversion.

DGEBA is relatively brittle with low stiffness. Mechanical properties of DGEBA can be enhanced by reinforcing carbon nanotubes (CNTs). The excellent mechanical properties of CNTs may be helpful in taking care of the inherent brittleness and low stiffness of epoxy DGEBA matrix. In last decades, CNT reinforced polymer matrix composites (PMCs) have been investigated for their superior strength to weight ratio and stiffness to weight ratio. CNTs have shown their high potential in improving the material properties of polymers

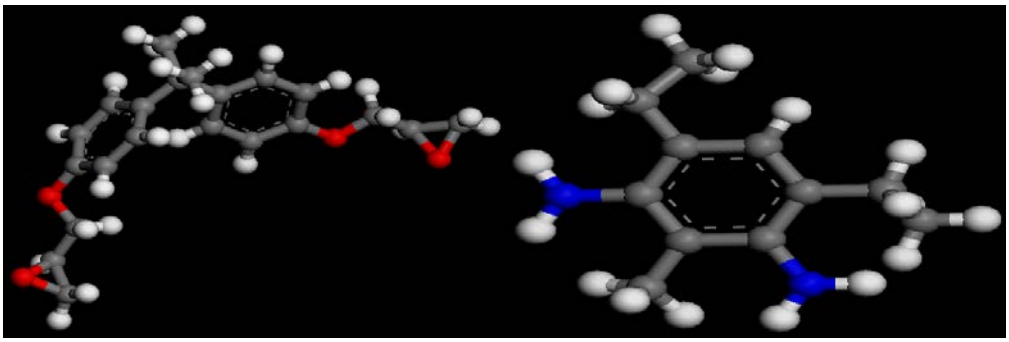
[9, 10]. Besides the improved electrical conductivity and thermal conductivity, the improvement of mechanical properties is of special interest. This originates from observations that CNTs with brittle materials may impart some of the attractive mechanical properties of the CNTs to the resulting composites. Thus, it makes CNTs an excellent candidate for reinforcement of polymeric materials [11, 12]. Numerous studies have been reported about the reinforcement of CNT and the characterization of CNT reinforced nanocomposites. Michael et al. [13] employed MD simulations to characterize elastic properties of polymer-carbon nanotube composites. Single-walled carbon nanotube was reinforced in polyethylene. Han et al. [14] had applied classical MD simulation on polymer/CNT composites, obtained by reinforcing single walled CNT into two different amorphous polymer matrices: poly (methyl methacrylate) and poly (m-phenylene-vinylene)-co-[(2, 5-dioctoxy-p-phenylene) vinylene] (PmPV), respectively, with different volume fractions. Rezaei et al. [15] investigated the influence of CNTs on the mechanical characteristics of amorphous metallic glasses by using molecular dynamics simulations. The authors had constructed long continuous and short discontinuous CNT-reinforced metallic glasses nanocomposites and determined their stress-strain responses and elastic modulus. Ahmed et al. [16] employed molecular dynamics simulations to estimate the elastic properties of SWCNT, interfacial bonding, polyethylene matrix and composites with aligned and randomly distributed SWCNTs.

Some studies on CNT composite materials were carried out experimentally, but the reinforcement theory is still not clear. In particular, during the mixture process of CNT-reinforced composites, some of the CNTs could be destroyed and the alignment of CNTs cannot be exactly straight. Therefore, analytical/numerical studies on the effective stiffness of the composites would be very helpful for understanding the reinforcement.

The purpose of the present investigation is to obtain the mechanical properties of epoxy DGEBA with and without reinforcement of CNT, based on molecular dynamics, using material studio. Chemically cross-linked rigid structure (triangular) has been model using the curing agent diethyl toluene diamine (DETDA). Representative composite models, called amorphous cell, have been created for both DGEBA and CNT reinforced DGEBA. Simulations have been carried out at room temperature and elevated temperature to study the effect of temperature on mechanical properties of composite.

2. Details of MD simulations

Building the atomistic models and oligomeric models. An atomistic model has been built using epoxy DGEBA and hardener DETDA. Molecules of DGEBA and DETDA are created in Material Studio software as shown in Fig. 1.



(a) (b)

Fig. 1. Atomistic structure of (a) epoxy, DGEBA, and (b) hardener, DETDA.

Product information from a manufacturer of DGEBA–DETDA resins states that the typical ratio of monomer to curing agent in the final resin is 100/26.4 by weight [17]. This

implies a number ratio of 2.15 normal DGEBA monomers to one DETDA molecule. Within this constraint, a triangle oligomer has been built shown in Fig. 2. The oligomer is built from seven DGEBA monomers and three DETDA molecules. The oligomeric model is created in the Materials Visualizer environment within the Materials Studio software.

The oligomer model (see Fig. 2) has been used to construct an amorphous cell, which has been taken as the representative composite for simulation purpose. This is a periodic simulation volume and constructed using Amorphous Cell module. To construct the amorphous, the density of the amorphous cell was kept lower than the target density. In case of DGEBA, target density is 1.20 g/cm^3 and density was kept 1.15 g/cm^3. The periodic cell length parameters were then decreased gradually following local energy minimization for each frame. The steps were repeated until the target density was achieved. The building process was followed by short (20 ps) trajectories of canonical and isothermal – isobaric molecular dynamics to stabilize the temperature and pressure near ambient condition, i.e. 298 K and 1 atm, respectively, before further dynamics runs. The building process was repeated multiple times for a given system, to provide: (i) a sampling of different starting points for the dynamics and (ii) a base for estimating uncertainties of the calculated properties.

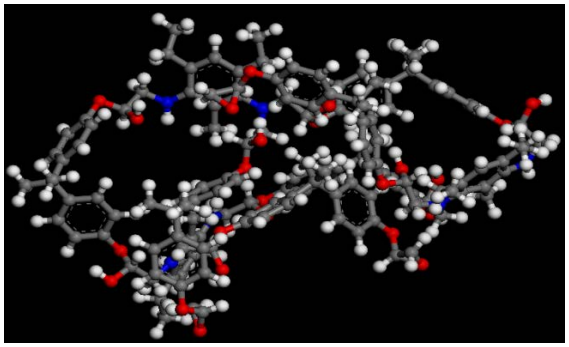


Fig. 2. Triangle oligomer model of DGEBA-DETDA.

Ten different frames of amorphous cell have been created and each frame consists of ten triangular oligomer model. Triangular model, packed into a periodic box, is shown in Fig. 3. Since the individual oligomers (Fig. 2) are somewhat two-dimensional by construction, one concern is that the final packed models might have unrealistic structural anisotropies (although the techniques of Amorphous Cell is designed to avoid this situation).

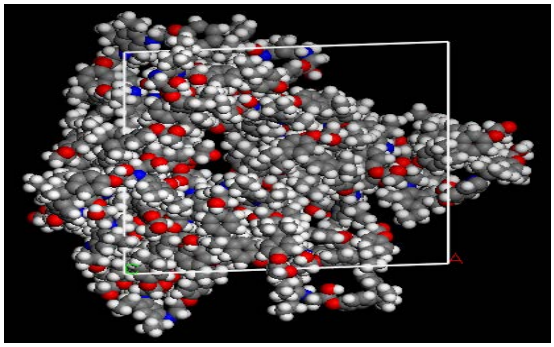


Fig. 3. Constructed amorphous cell of DGEBA, cured with DETDA.

Reinforcement of SWCNT in epoxy matrix. Carbon nanotubes (CNTs) are considered as potential fillers to improve the material properties of epoxy. CNTs exhibit an exceptionally high stiffness and strength. According to their graphitic structure, CNTs possess a high thermal conductivity and an electrical conductivity. The mechanical properties of epoxy can be improved drastically at reinforcement of CNT. In the present research, armchair SWCNT (10 10) has been introduced into the epoxy (DGEBA) matrix. The DGEBA monomers, cured with DETDA, have been densely packed around the SWCNT by creating the iso-surface in a periodic boundary cell. The molar ratio of the epoxy is 10. Reinforced model of CNT-epoxy model is shown in Fig. 4, indicating Vander wall's distance between epoxy and CNT.

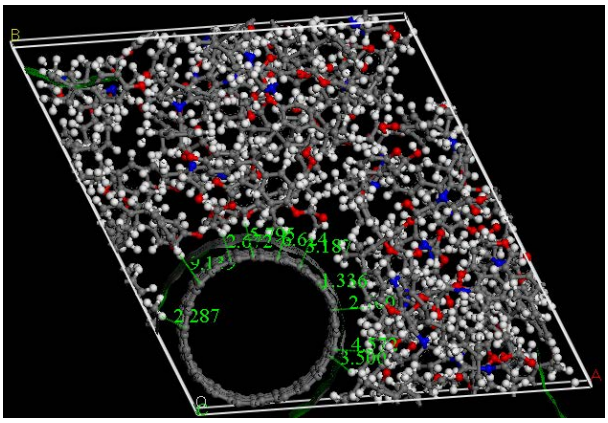


Fig. 4. CNT reinforced epoxy composite, indicating Vander wall's distance between epoxy and CNT.

3. Simulation methodology

Molecular dynamics simulation has been performed on the Forcite modules of the Material Studio software. Forcite has several advantages, including access to the proprietary COMPASS II force-field, support for non-orthombic simulation boxes and simplicity in importing the molecular model. After generating the initial coordinates of the amorphous cell, smart algorithm has been used. Smart algorithm is combination of conjugate gradient algorithm and steepest descent method for the energy minimization. It has been employed for 10,000 steps, followed by four stages (10,000 steps each) of MD following velocity rescaling in every time step using incrementally larger time steps (up to 1 fs time step size) to carefully remove any lingering initial bad contacts. Initially, the created amorphous cell has defects like vacuum voids and random orientation of molecule inside the cell. To remove these types of stability a geometry relaxation has been employed to relax the structure. After relaxing the structure Forcite dynamic simulation has been performed to achieve the desired density of the amorphous cell. Isobaric-isothermal (NPT) ensemble has been employed and pressure was 0.5 GPa. The simulation time step was 1 fs and the time duration was of 5 ps. From the results of the simulation, it has been seen that the developed model achieved the desired density i.e. 1.91 g/cm^3, which is very close to the actual density of the epoxy i.e. 1.2 g/cm^3, shown in Fig. 5.

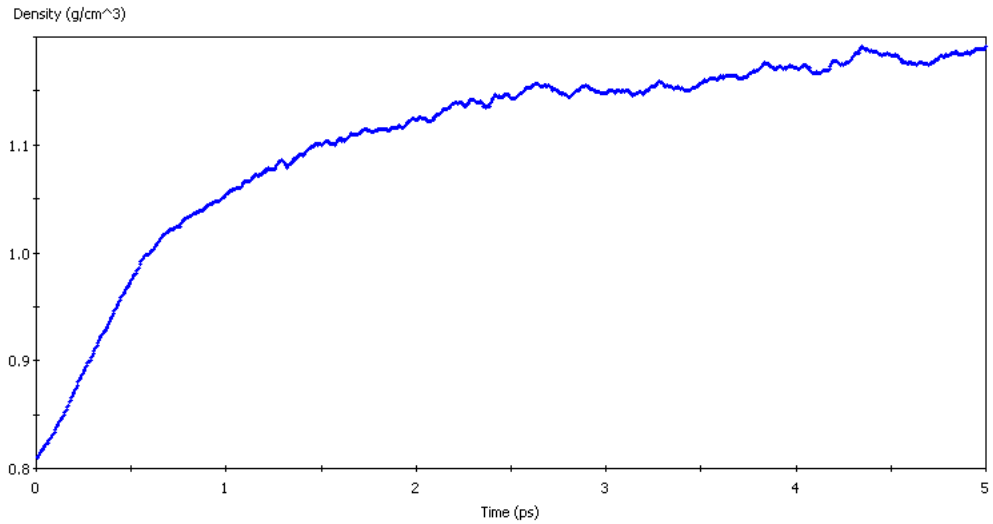


Fig. 5. Density (g/cm^3) *vs* time (ps) of DGEBA, cured with DETDA.

4. Results and discussions

To calculate the mechanical (elastic) properties of the developed epoxy composite (triangular model) and CNT reinforced epoxy composite, target density and thermodynamic stability of epoxy DGEBA and CNT reinforced DGEBA have been evaluated using Forcite dynamics with the parameters, mentioned in Table 1. By imposing the conditions and carrying out the iterations several times, the target density has been achieved shown in Fig. 5.

Table 1. Forcite geometry optimization and dynamics simulation process.

Geometry optimization		Dynamics simulation process	
Algorithm	Smart	Ensemble	NPT
Quality	Medium	Thermostat	Berendsen
Energy	0.001 kcal/mol	Barostat	Berendsen
Force	0.5 kcal/mol/Å	Initial velocity	Random
Maximum iterations	5000	Temperature	298 K
External pressure	1 atm	Pressure	0.5 GPa
		Time step	1 fs
		Total simulation time	5 ps
		Number of steps	20000

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 Forcite module. All the simulations have been performed at 298 K and 350 K using the triangular model with reduced number of molecules as described in Section 2. The 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 are 2.429 GPa and 2.184 GPa for 298 K and 350 K temperature, respectively, and Poisson's ratios are 0.42 and 0.40, respectively. The obtained results are similar to results, reported by Clancy et al. [18], which is 2.52 GPa and 2.2 GPa at temperature 300 K and 350 K, respectively, using the AMBER force-field on the epoxy DGEBA, cured with DETDA.

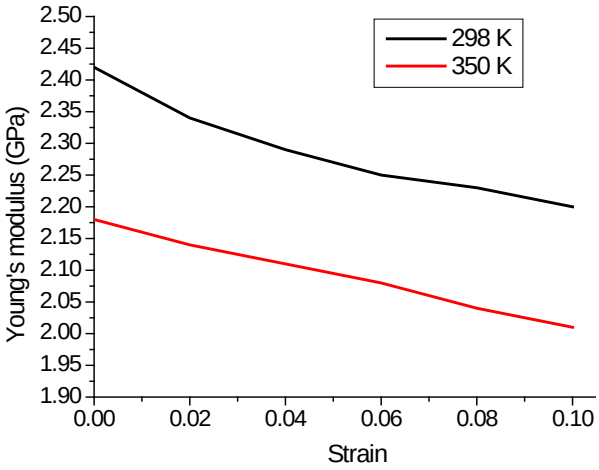


Fig. 6. MD simulated comparison of Young's modulus *vs* strain curves at temperature 298 K and 350 K.

The plot of Young's modulus of cured DGEBA at temperature 298 K and 350 K versus strain is shown in Fig. 6. From Fig. 6 it can be observed that the Young's modulus of cured DGEBA decreases with increasing strain. From Fig. 6, it can be also observed that at increase in temperature, the Young's modulus of the epoxy DGEBA decreases consistently. Fig. 7 shows stress-strain plot at two different temperatures 298 K and 350 K. It has been observed that up to the 2% of strain, there is no significant change in the value of stress but if we increase the strain percentage further, there is significant change in the stress.

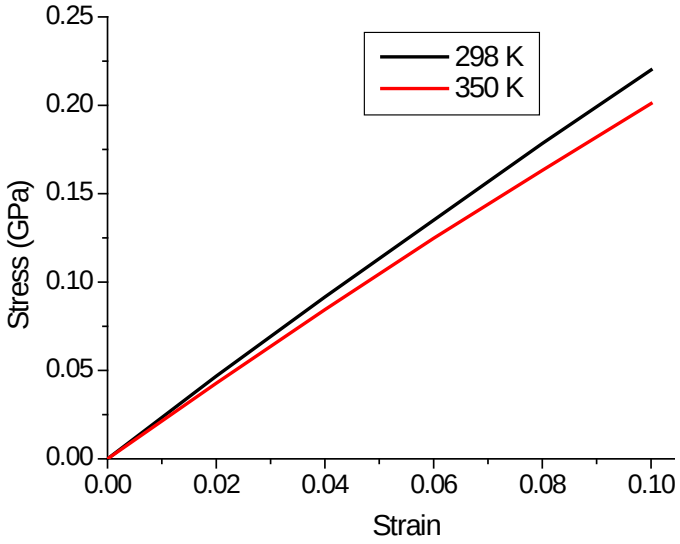


Fig. 7. MD simulated comparison of stress-strain curves at 298 K and 350 K.

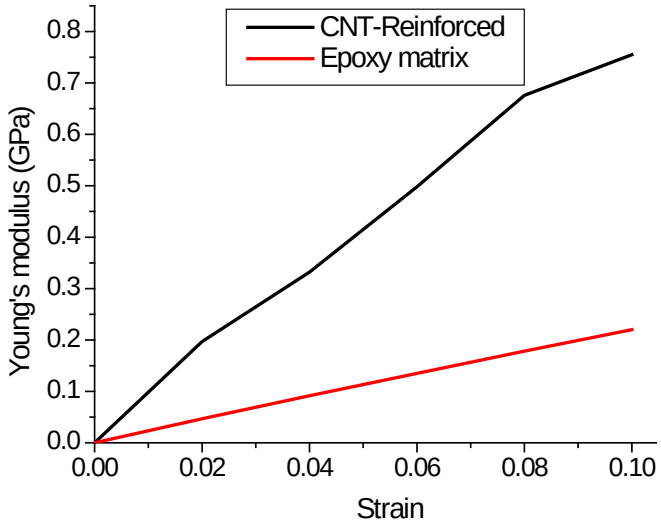


Fig. 8. Variation of MD simulated stress-strain curves of epoxy matrix and CNT reinforced epoxy.

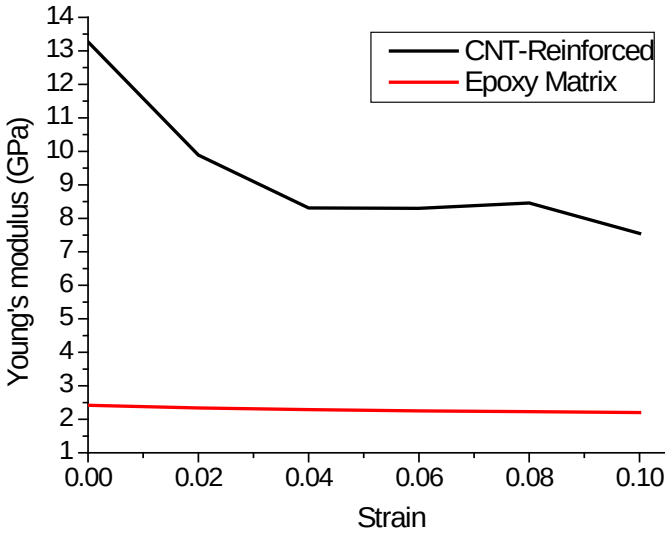


Fig. 9. Variation of MD simulated Young's moduli of epoxy matrix and CNT reinforced epoxy with increasing strain.

The elastic properties of CNT reinforcement epoxy DGEBA is shown in Fig. 8 and Fig. 9 at room temperature i.e. 298 K. From Fig. 8, it can be seen that the stress-strain curve is almost linear. Under the same strain, the stress in the CNT reinforced composite is much larger than the epoxy matrix. From Fig. 9, it can be observed that reinforcement of CNT in the epoxy matrix substantially enhances the composite stiffness.

5. Conclusions

Molecular Dynamics simulations has been employed to study the elastic properties of the epoxy DGEBA cured with DETDA, CNT reinforced epoxy/CNT composite. The following conclusion is observed from the present study:

The two models of composites have been investigated: (a) epoxy matrix with CNT reinforcement and (b) without CNT reinforcement. The predicted MD simulations results for epoxy DGEBA-DETDA indicate that the Young's modulus decreases consistently with increase in temperature. The Young's moduli (slopes of the stress-strain curves) of the epoxy DGEBA cured with DETDA decreases with the increasing strain levels. The MD simulated

result indicate clearly that, the Young's modulus (slope of stress-strain curve) of the reinforced composites or the epoxy matrix decrease with increase in strain levels (from 0.0 to 0.1). Most importantly, the MD results shows that at any given strain level CNT reinforced epoxy composite is 5 times stiffer than the pure epoxy matrix.

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