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Simulation and comparison of DGEBF/TETA epoxy system with cross linking

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ABSTRACT

Thermoset polymers are in commanding position as matrix material in making polymer composites due to its low cost, good thermal and mechanical properties and fibre bonding. By using polymer matrix, the weight of the component can be reduced and in many cases, it is the primary application. The properties of the matrix have a significant effect on the behavior of composite materials. Therefore, it is important to have the knowledge of properties of polymers. In the present Analysis, molecular dynamic simulations were conducted for the prediction of thermal and mechanical properties of epoxy system consists of DGEBF epoxy resin and TETA as a curing agent. For this we used software LAMMPS cross linking density of epoxy system is varied and properties such as young's modulus, shear modulus, poisson's ratio and glass transition temperature are estimated. The young's modulus and shear modulus obtained are in accordance with the previous literature. The results noticed that the young's modulus, shear modulus and glass transition temperature increases as the percentage of cross linking density increases. For this kind of analysis another software can also be used e.g. COSMOS, ENCAD, GROMOS, GROMACS etc.,

Keywords: Matrix material**,** Polymers, DGEBF Epoxy resins and TETA, LAMMPS, Cross Linking

INTRODUCTION

Composite materials consist of two or more materials which are called reinforcements and matrix. The strength of the new material is better than the individual materials, indeed it is the reason of making composites. Most often in composites the weakness of the one material is covered by the other material. The matrix acts as a binder and transfer loads to the fibres. It also maintains the orientation of fibres and distributes the loads. For selecting the matrix components certain considerations like stiffness, yield and ultimate strength, cost availability, thermal and toughness properties has to be concerned. For processing of metal and ceramics high temperature and high pressures are required and also, they are more expensive than polymer matrix. Yet the thermal stability of ceramic and metal composites is better and are used where the composite applications are prone to high temperatures. Materials can be isotropic or anisotropic. At a given point if the properties are same in all directions, it is an isotropic material. If the properties are different in all directions it is an anisotropic material. In most cases, the primary application of composite is to reduce weight in components, the material engineers and structural designers are looking for better resin systems. The low cost, good thermal and mechanical properties, good fibre bonding reasoned.

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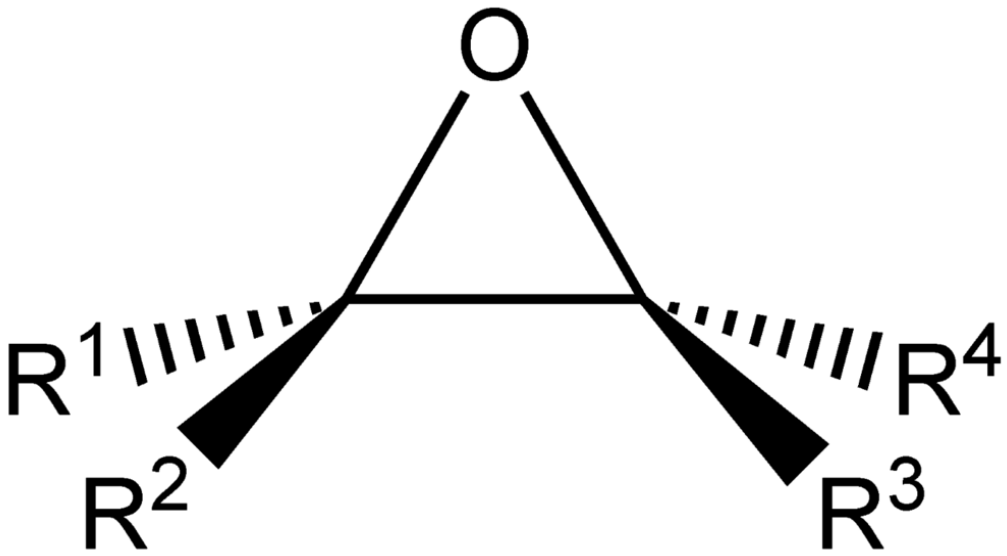


Figure 1: Epoxide Generic Structure

OBJECTIVE

The cross linking density effects the properties of the epoxy system. To the authors knowledge, there is no study regarding the prediction of properties by varying the cross linking density of DGEBF cured with TETA epoxy system. It is also known that the glass transition temperature can be further improved by the addition of DGES epoxy to other epoxides, but the influence of DGES in mechanical properties is not yet known. Therefore, the current analysis addresses these issues using molecular dynamic simulations. Based on this the following objections are drawn.

1. Build and validate the model of DGEBF and TETA epoxy system with the already available results.
2. Study the effects of cross linking density of DGEBF and TETA epoxy system on thermal and mechanical properties.
3. Study the effect of percentage addition of SEP epoxy resin in DGEBF- TETA epoxy system on the performance properties such as thermal and mechanical properties.
4. Comparison of DGEFA/TETA epoxy system with other epoxy systems

MOLECULAR DYNAMICS SIMULATIONS

Molecular dynamics (MD) is a computer simulation method for studying the physical movements of atoms and molecules. The atoms and molecules are allowed to interact for a fixed period of time, giving a view of the dynamic evolution of the system. In the most common version, the trajectories of atoms and molecules are determined by numerically solving Newton's equations of motion for a system of interacting particles, where forces between the particles and their potential energies are often calculated using inter atomic potentials or molecular mechanics force fields.

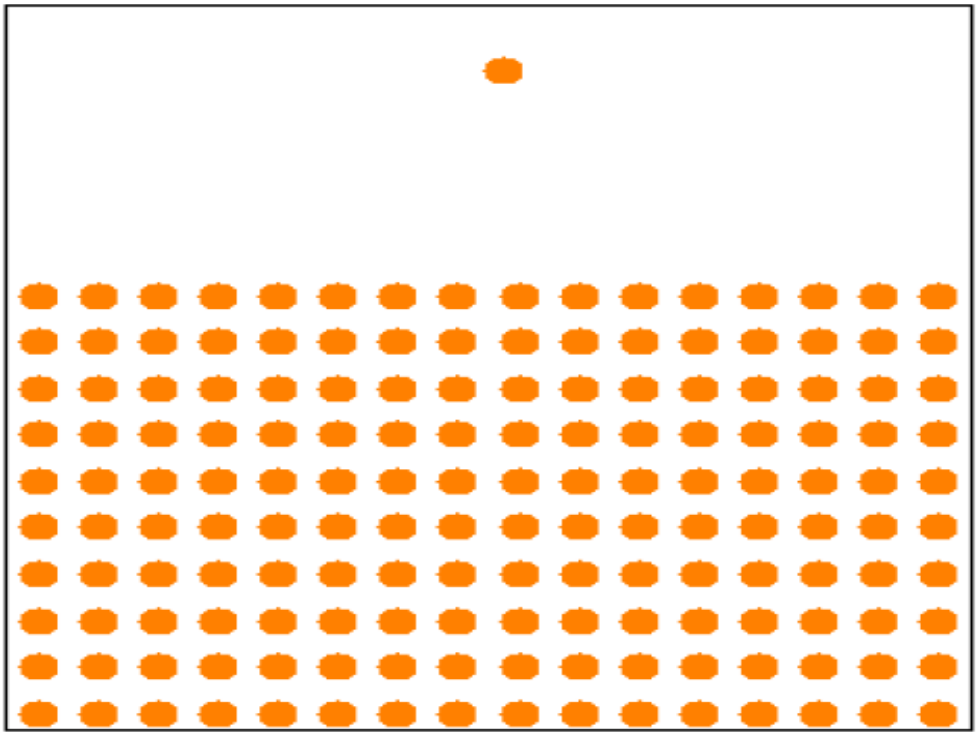


Fig-2 Deposition of one copper (Cu) atom on a Cu Miller index (001) surface.

Design of a molecular dynamics simulation should account for the available computational power. Simulation size (n = number of particles), time step, and total time duration must be selected so that the calculation can finish within a reasonable time period. However, the simulations should be long enough to be relevant to the time scales of the natural processes being studied. To make statistically valid conclusions from the simulations, the time span simulated should match the kinetics of the natural process. Otherwise, it is analogous to making conclusions about how a human walks when only looking at less than one footstep. Most scientific publications about the dynamics of proteins and DNA use data from simulations spanning nanoseconds (10−9 s) to microseconds (10−6 s). To obtain these simulations, several CPU-days to CPU-years are needed. Parallel algorithms allow the load to be distributed among CPUs; an example is the spatial or force decomposition algorithm. During a classical MD simulation, the most CPU intensive task is the evaluation of the potential as a function of the particles' internal coordinates. Within that energy evaluation, the most expensive one is the non-bonded or non-covalent part. In Big O notation, common molecular dynamics simulations scale by if all pair-wise electrostatic and van der Waals interactions must be accounted for explicitly. This computational cost can be reduced by employing electrostatics methods such as particle mesh Ewald summation (O(nlog(n)), particle–particle-particle–mesh (P3M), or good spherical cut off methods (O(n^2)).

Isothermal–isobaric (NPT) ensemble

In the isothermal–isobaric ensemble, amount of substance (N), pressure (P) and temperature (T) are conserved. In addition to a thermostat, a barostat is needed. It corresponds most closely to laboratory conditions with a flask open to ambient temperature and pressure. In the simulation of biological membranes, isotropic pressure control is not appropriate. For lipid bi layers, pressure control occurs under constant membrane area (NPAT) or constant surface tension "gamma" (NPγT).

Potentials in MD simulations

A molecular dynamics simulation requires the definition of a potential function, or a description of the terms by which the particles in the

simulation will interact. In chemistry and biology this is usually referred to as a force field and in materials physics as an inter atomic potential. Potentials may be defined at many levels of physical accuracy; those most commonly used in chemistry are based on molecular mechanics and embody a classical mechanics treatment of particle-particle interactions that can reproduce structural and conformational changes but usually cannot reproduce chemical reactions. The reduction from a fully quantum description to a classical potential entails two main approximations. The first one is the Born–Oppenheimer approximation, which states that the dynamics of electrons are so fast that they can be considered to react instantaneously to the motion of their nuclei. As a consequence, they may be treated separately. as point particles that follow classical Newtonian dynamics. In classical molecular dynamics, the effect of the electrons is approximated as one potential energy surface, usually representing the ground state. When finer levels of detail are needed, potentials based on quantum mechanics are used; some methods attempt to create hybrid classical/quantum potentials where the bulk of the system is treated classically but a small region is treated as a quantum system, usually undergoing a chemical transformation.

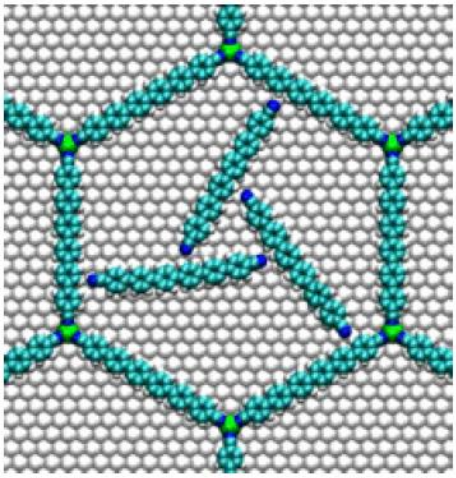
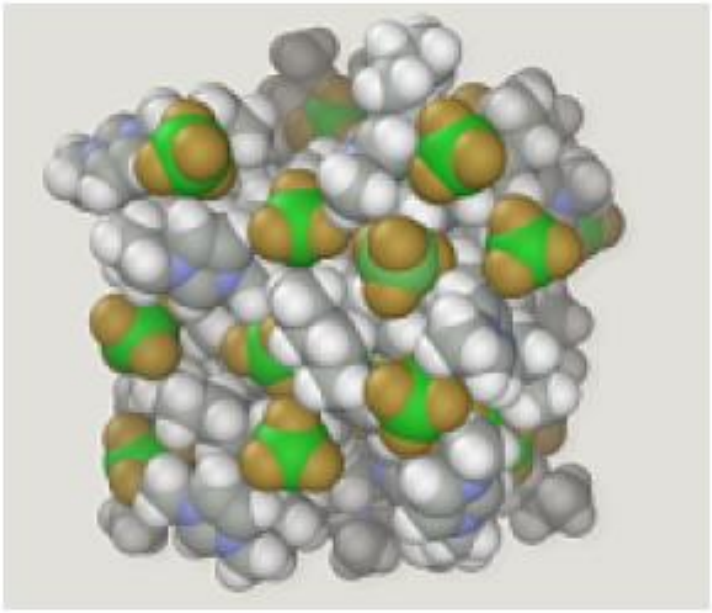


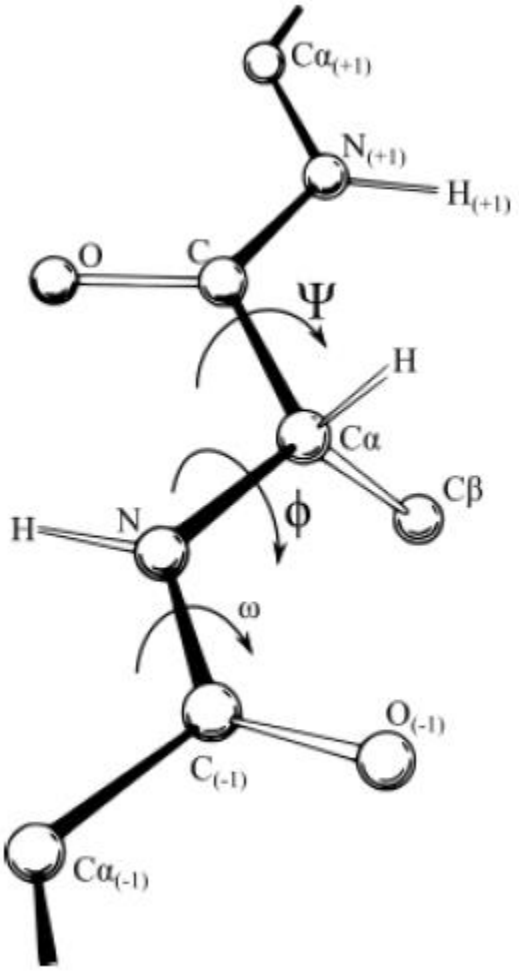
Fig-3: Molecular dynamics simulation of a synthetic molecular motor composed of three molecules in a nano pore (outer diameter 6.7 nm) at 250 K.

MOLECULAR MODELLING

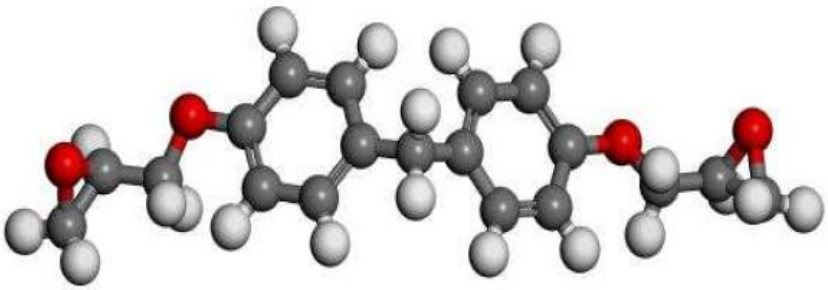
Molecular modelling encompasses all methods, theoretical and computational, used to model or mimic the behaviour of molecules. The methods are used in the fields of computational chemistry, drug design, computational biology and materials science to study molecular systems ranging from small chemical systems to large biological molecules and material assemblies. The simplest calculations can be performed by hand, but inevitably computers are required to perform molecular modelling of any reasonably sized system. The common feature of molecular modelling methods is the atomistic level description of the molecular systems. This may include treating atoms as the smallest individual unit (a molecular mechanics approach), or explicitly modelling electrons of each atom (a quantum chemistry approach).



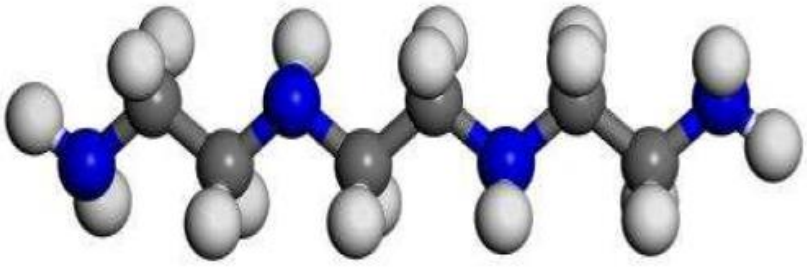
Modeling of ionic liquid



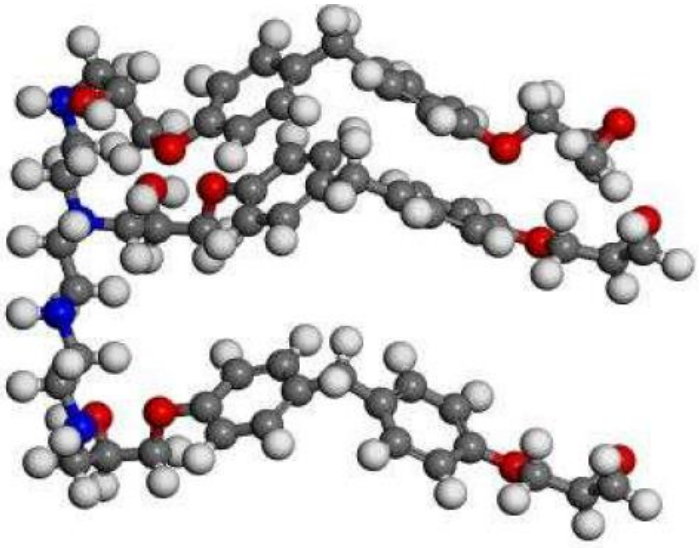
The backbone dihedral angles are included in the molecular model of a protein



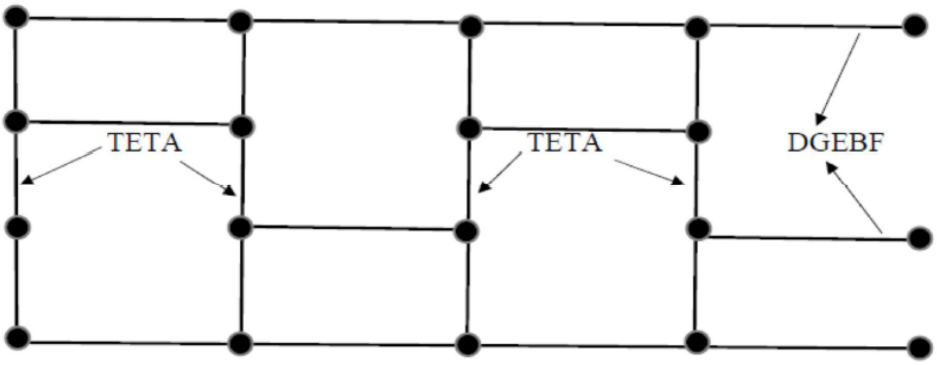
Molecular structure of diglcyl ether bisphenol F (DGEBF)



Molecular structure of tri ethylene tetramine (TETA)



Molecular structure of DGEBF bonding with TETA at three reactive sites.

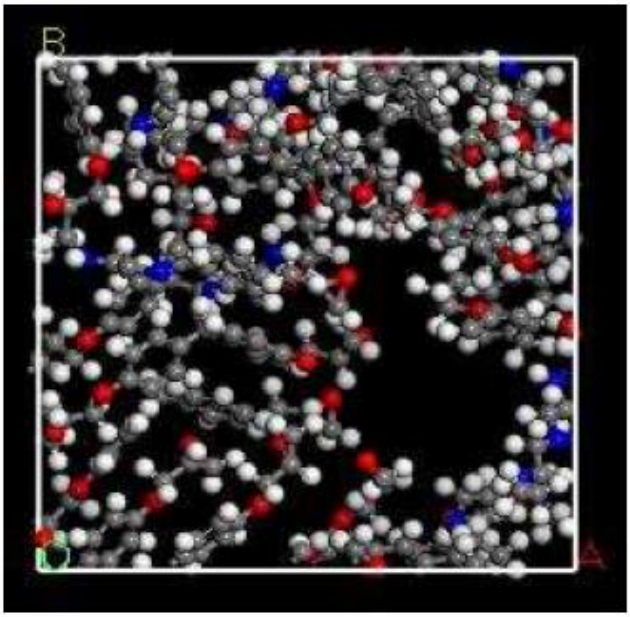


Line structure of DGEBF and TETA molecules forming 87.5% cross linking density.

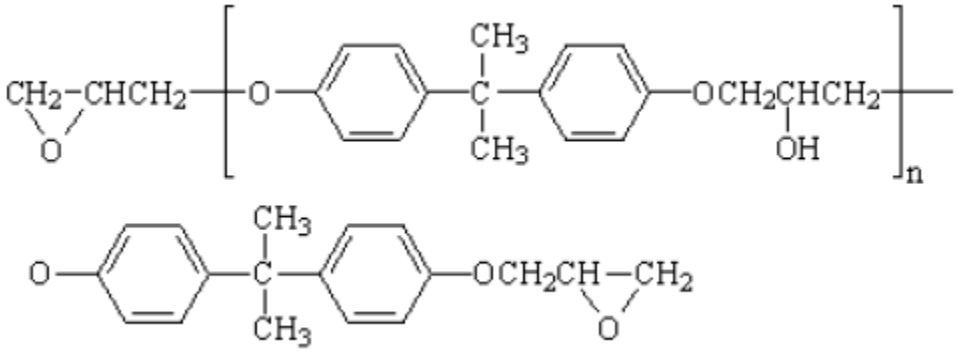
SIMULATION OF DGEFA/TETA

The system is initially constructed with a density of 0.5 g/cm3 at the room temperature by applying periodic boundary conditions. Periodic boundary conditions are considered so that the effects due to surfaces are not considered. After construction, Geometrical optimization is done by steepest descent method followed by conjugate gradient method for 50,000 minimization steps so that the available energy reached is minimum.

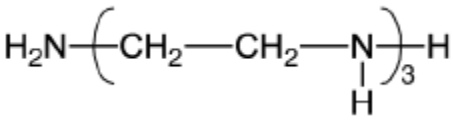
The Figure shows the initial construction of epoxy system, with the molecules forming 50% of cross linking density. When the system is constructed primarily it occupies a volume of 24.32×24.32 × 24.32 Ao3, for 12 DGEBF and 4 TETA molecules reacted with 50% cross linking density.



Initial model construction

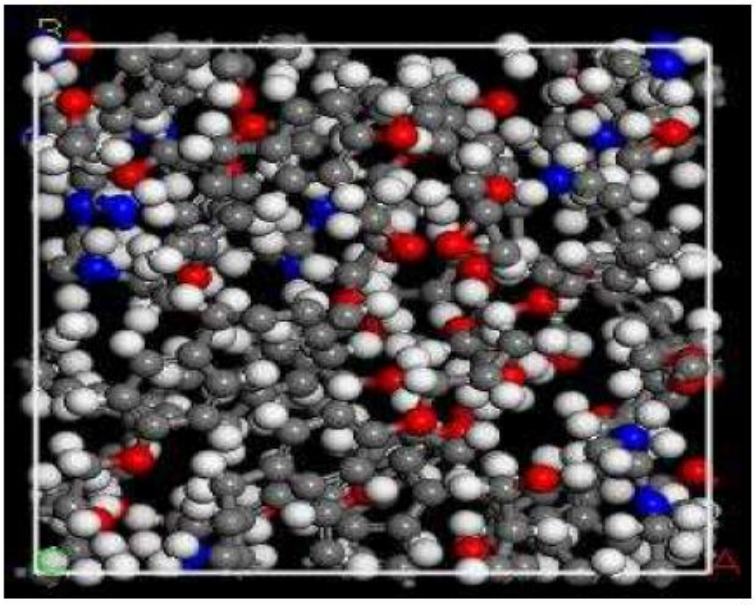


Chemical structures of the resin DGEBF

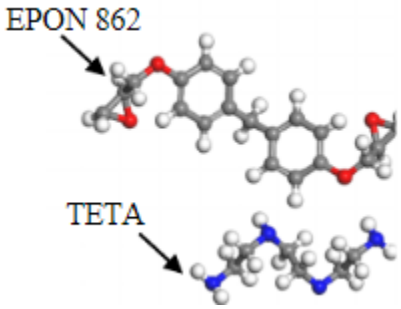


Chemical structures of the resin TETA

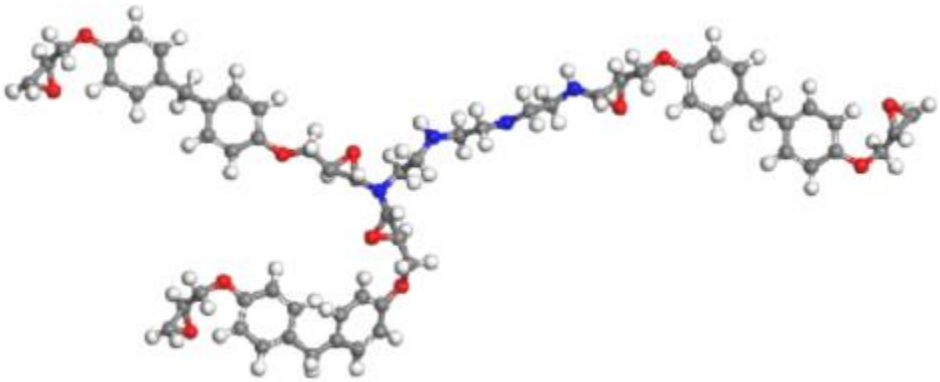
A minimisation is performed using smart minimiser in order to release stress formed duringNPT dynamics. Followed by NVT for 200ps a NPT calculation for 1000 ps is performed at a timestep of 1 fs at 1atm pressure and 298 K temperature to establish a stable configuration forcalculation of properties. After the system reaches stable configuration, it acquires a volume of18.18×18.18×18.18 Ao3, the Fig.12 shows the final layout of the epoxy system.



Final equilibrium model



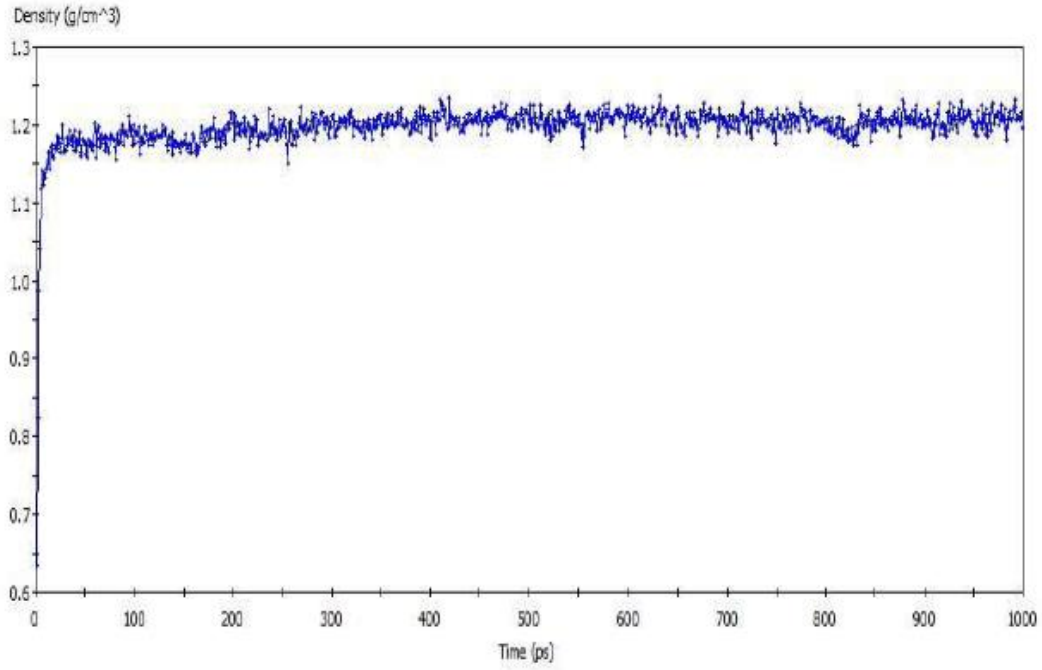
Molecular model of DGEBF (EPON 862) and TETA



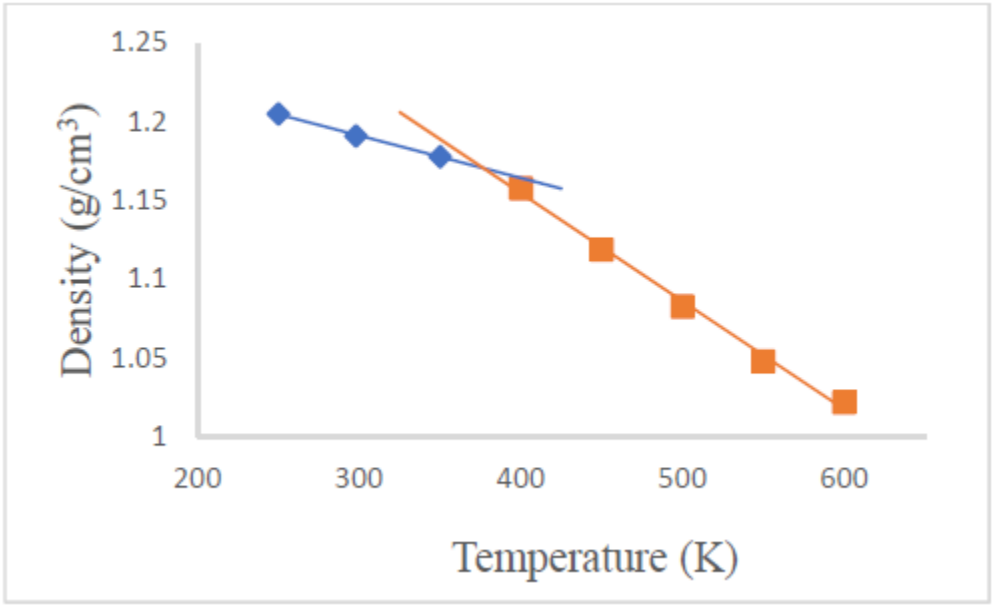
Cross Linked Epoxy.

RESULTS

The model/system is constructed with DGEBF and TETA epoxy system at 50% crosslinking density as given by Suyoung Yu and then the geometrical optimization is done to bring the system to least energy minimised state.



Density vs Time



Density vs Temperature plot at 50% crosslinking density

The stiffness matrix obtained based on the calculations of COMPASS force field is as follows

$$Cij = \begin{bmatrix} 6.5888 & 4.5668 & 4.4791 & 0.0834 & -0.1887 & 0.1544 \\ 4.5668 & 6.8123 & 4.2168 & -0.1570 & 0.7782 & -0.5810 \\ 4.4791 & 4.2168 & 5.4380 & -0.2778 & 0.1007 & 0.0516 \\ 0.0834 & -0.1570 & -0.2778 & 1.2417 & 0.5766 & 0.4355 \\ -0.1887 & 0.7782 & 0.1007 & 0.5766 & 1.0676 & 0.4411 \\ 0.1544 & -0.5810 & 0.0516 & 0.4355 & 0.4411 & 1.3797 \end{bmatrix} \quad (4.1)$$

Table.1 Mechanical properties for 50% crosslinking density

Mechanical Properties	Present result	Previous result [14]
Young's modulus (E) (GPa)	3.3937	3.362
Shear modulus (G) (GPa)	1.2297	1.222

Comparison of DGEFA/TETA epoxy system with other epoxy systems:

As we are proving that TETA is has got good efficiency in terms of epoxy system range as compared with other epoxy systems. It is much stronger and got capable of storing more energy. For this is case it compared with DETA of same range. As this results we are comparing with DGEFA/DETA by B. Arab (31.15.at, 61.25.hp, 82.35.Lr).

Results of DETA are as follows

COMPASS:

$$C_{ij} = \begin{pmatrix} 4.68 & 2.13 & 1.95 & 0.01 & 0.01 & -0.07 \\ 2.13 & 5.25 & 2.49 & -0.01 & 0.06 & 0.01 \\ 1.95 & 2.49 & 5.11 & -0.20 & 0.06 & -0.09 \\ 0.01 & -0.01 & -0.20 & 1.30 & -0.07 & 0.03 \\ 0.01 & -0.83 & 0.06 & 0.06 & -0.07 & 1.25 \\ -0.07 & 0.01 & -0.09 & 0.03 & 0.04 & 1.35 \end{pmatrix}$$

PCFF:

$$\lambda_{ij} = \begin{pmatrix} 4.52 & 2.37 & 2.38 & -0.10 & -0.03 & 0.05 \\ 2.37 & 4.82 & 2.43 & -0.12 & 0.03 & 0.10 \\ 2.38 & 2.43 & 4.71 & 0.08 & -0.28 & 0.06 \\ -0.10 & -0.12 & 0.08 & 1.09 & 0.11 & -0.02 \\ -0.03 & 0.03 & -0.28 & 0.11 & 1.24 & 0.03 \\ 0.05 & 0.10 & 0.06 & -0.02 & 0.03 & 1.23 \end{pmatrix}$$

UFF:

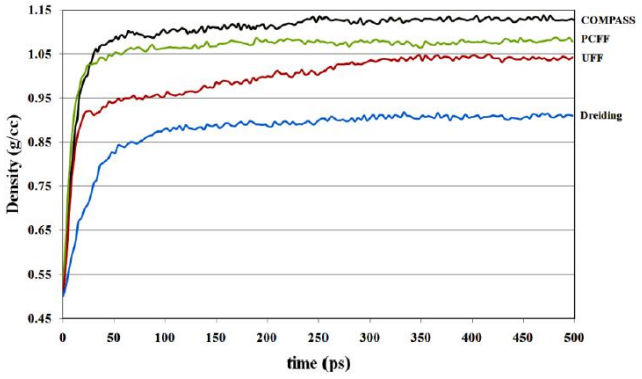
$$\lambda_{ij} = \begin{pmatrix} 5.51 & 2.50 & 1.79 & 0.32 & -0.24 & -0.08 \\ 2.50 & 5.64 & 2.23 & 0.26 & -0.08 & -0.46 \\ 1.79 & 2.23 & 5.24 & 0.11 & 0.21 & -0.30 \\ 0.32 & 0.26 & 0.11 & 1.61 & -0.06 & -0.02 \\ -0.24 & -0.08 & 0.21 & -0.06 & 1.84 & -0.08 \\ 0.08 & -0.46 & -0.30 & -0.02 & -0.09 & 1.60 \end{pmatrix}$$

Dreiding:

$$C_{ij} = \begin{pmatrix} 3.01 & 1.34 & 1.22 & -0.21 & -0.18 & -0.35 \\ 1.34 & 3.23 & 1.09 & 0.08 & -0.34 & -0.27 \\ 1.22 & 1.09 & 3.12 & -0.28 & -0.09 & -0.14 \\ -0.21 & 0.08 & -0.28 & 0.59 & 0.03 & -0.07 \\ -0.18 & -0.34 & -0.09 & 0.03 & 0.89 & -0.04 \\ -0.35 & -0.27 & -0.14 & -0.07 & -0.04 & 1.01 \end{pmatrix}$$

Mechanical properties of the cross-linked epoxy from MD simulations, using different force fields, in comparison with experimental data (all moduli are in GPa).

Property	Simulations results				Experimental results
	Compass	PCFF	UFF	Dreiding	
Young's modulus, E	3.44	3.16	4.30	2.19	3.05 – 3.86 [51-53]
Shear modulus, G	1.3	1.19	1.68	0.83	–
Bulk modulus, K	3.28	3.10	3.22	2.01	–
Poisson's ratio, ν	0.32	0.33	0.28	0.32	0.36 ± 0.06 [53]
Density, g/cm³	1.11	1.08	1.05	0.91	1.16 [51], 1.19 [54]



CONCLUSIONS

Molecular dynamic simulations are carried out for the Analysis of material properties for varied cross linking density of DGEBF and TETA epoxy system using software LAMMPS.

For different cross linking densities, material properties such as young's modulus, shear modulus, poisson's ratio and glass transition temperature are determined.

The present work provides the following outcomes. Young's moduli obtained from the present study are in accordance with the previous investigation values indicates that the molecular dynamic procedure followed is reliable.

- The increase in cross linking density provides better material properties.
- I have compare TETA with DETA COMPASS (Field Force) is approximate and reliable.

Future work

Molecular dynamic simulation can be extended to study the material properties of the epoxy system by adding nano-particles for various cross linking densities. The effects in the properties of an epoxy system could be known when mixed with other epoxy resins.

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