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A Molecular Dynamic Modelling of Cross-Linked Epoxy Resin Using Reactive Force Field: Thermo-Mechanical Properties

Olanrewaju Aluko[1], S. Gotham[2] and G. M. Odegard[2]

1. Department of CSEP, College of Arts and Science, University of Michigan-Flint, Flint, MI 48502, USA

2. Department of Mechanical Engineering & Engineering Mechanics, Michigan Technological University, Houghton, MI 49931, USA

Abstract: The reactive force field was used to study the molecular dynamics of cross-linked EPON 862 (diglycidyl ether of bisphenol-F) and DETDA (diethylene toluene diamine) system in order to predict its thermo-mechanical behavior under different loading conditions. The approach for building the EPON 862/DETDA structures, cross-linking, and equilibration of the systems, and the evaluation of the models are presented. The mechanical properties such as Young's and shear moduli, Poisson ratio, and yields strength as well as thermal properties such as glass transition temperature and coefficient of thermal expansion are predicted. The results are in close agreement with both experimental data and simulated results in literature.

Key words: Reactive force field, molecular dynamics, thermo-mechanical, equilibration.

1. Introduction

Materials that have specific and unusual properties are needed for a host of high-technology applications such as those found in the aerospace, underwater, bio-engineering, and transportation industries Therefore, the engineering needs for fiber-reinforced composites with polymeric matrices continues to increase as engineers seek specialized materials with superior mechanical properties that can be tailored to support the requirements of structural components. In light of this, fiber-reinforced epoxy composite materials have received the attention of many researchers [1-15] due to their formidable combination of characteristics such as high specific modulus and strength, good compatibility between the fibers and epoxy materials and low weight. The performance of epoxy based materials can be further improved through computational molecular dynamics studies under different force fields. Varshney et al. [1] utilized CVFF (consistent valence force field) to study cross-linking procedure and predict molecular and material properties of epoxy-based thermoset (EPON 862/DETDA). Different approaches to build highly cross-linked polymer network are discussed and a multistep relaxation procedure for relaxing the molecular topology during cross-linking was presented. They calculated several material properties such as density, glass transition temperature, thermal expansion coefficient, and volume shrinkage during curing and their results were in agreement with experimental data.

Li and Strachan [2] used molecular dynamics with a procedure to describe chemical reactions to predict the atomic structure and properties of the thermosetting polymer epoxy (EPON-862) and curing agent (DETDA). The DREIDING force field is employed with environment-dependent atomic charges obtained self consistently during the dynamics. They proposed a computationally efficient method to describe charge

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Corresponding author: Olanrewaju Aluko, Ph.D., assoc. professor, research fields: mechanics of advanced materials and nanocomposites.

evolution based on the observation that atomic charges evolve significantly only during chemical reactions and in a repeatable manner. They used two chemistry models with different relative rates for primary and secondary amine reactions to mimic the curing process in two extreme cases of processing conditions. Their simulations showed that differences in chemical reaction rates of interest affect properties for intermediate conversion degrees (~40-70%) but not for the higher conversion rates of interest in most applications. The predicted density, coefficient of thermal expansion, glass transition temperature and elastic constants of the resulting polymers are in agreement with experiments. Abbott et al. [3] presented a generalized structure generation methodology for amorphous polymers by a simulated polymerization technique and 21-step molecular dynamics equilibration, which is particularly effective for high-T_g polymers. Validation of the methodology is provided by comparison of the simulations and experiments for a variety of structural, adsorption, and thermal properties, all of which showed excellent agreement with available experimental data.

Doherty et al. [4] described a methodology to build cross-linked atomistic structures for poly(methacrylate). They performed simulations allowing a progressive crosslinking and polymerization reaction using molecular dynamics. They also used an explicit velocity rescaling molecular dynamics algorithm to relax the local energetic stresses caused by bond formation. However, the obtained network structure from their analysis was not characterized for mechanical properties because that was not the focus of their study. Other computational studies [5, 6] involving crosslinking of epoxies have been performed on relatively small model systems (less than 2,200 atoms).

Yarovsky and Evans [7] developed a methodology that was applied to low molecular weight water soluble epoxy resins cross-linked with different curing agents that are being considered for use as a primer coating on steel. Their simulations allowed the crosslink density and the amount of free crosslinking sites in the coatings to be predicted. Shrinkage of the resin upon curing was reproduced by the simulation and the barrier properties of model coatings were estimated. Their developed methodology has a potential to significantly impact on the design and development of new coatings with improved barrier and adhesion properties.

Wu and Xu [8] performed crosslinking simulations for epoxy resin system based on DGEBA (diglycidyl ether bisphenol A) and IPD (isophorone diamine). They used the DREIDING force field with charge equilibration to build the structure but COMPASS force field for property prediction. They found that COMPASS provides a more accurate description of elastic properties. Their DREIDING prediction of Young's modulus (about 50 GPa) is not in good agreement with the result of Li et al. [2] who utilized the same force field to obtain Young's' modulus in the range 3.2-3.5 GPa.

Littell et al. [9] conducted experimental tests using small test specimens on epoxy resin in tension, compression, and shear over a wide range of strain rate and their results have been found to be very useful as benchmark for simulated results. Komarov et al. [10] documented a new computational method where the polymer network is polymerized at a coarse-grained level and then mapped into a fully atomistic model. Molecular dynamics are then carried out with the OPLS force field. The predicted T_g is about 20 K lower than that of experimental results; this underestimation would increase once the extremely high cooling rates of MD taken into account.

Lin et al. [11] reported a single-step polymerization method for the creation of atomistic model structures of cross-linked polymers. A simulated annealing algorithm was used to identify pairs of reacting atoms within a cutoff distance and all crosslinking bonds were created in a single step. Bandyopadhyay et al.

[12] applied molecular dynamics and molecular mechanics simulation to establish well-equilibrated, validated molecular models of the EPON862-DETDA epoxy system with a range of crosslink densities using a united atom force field. Their models were used to predict glass transition temperature, thermal expansion coefficients, and elastic properties of each of the crosslink systems. The results indicate that glass transition temperature and elastic properties increase with increasing levels of crosslink density and the thermal expansion coefficient decreases with crosslink density, both above and below T_g temperature. Their results also demonstrated reasonable agreement with thermomechanical properties in literature.

Aluko et al. [13] utilized the molecular dynamics model using all atoms OPLS force field to estimate the thermo-mechanical response of epoxy-based network. They compared the simulated mechanical properties as well as the thermal properties with both the computational and experimental data in literature and found the model to be excellent.

As stated in Ref. [14], the ReaxFF (reactive force field) was initially developed to model bond dissociation and formation in carbon-based materials [15]. In the ReaxFF, the potential energy is defined as a function of bond order with energy penalties for nonequilibrium configurations. Odegard et al. [14] utilized the application of reactive force field (ReaxFF) to the molecular dynamics simulations of cross-linked epoxies. Their results demonstrated that mechanical stiffness and the obtained values of Pisson's ratio showed a close agreement with experiment. Their results also indicated that despite the inherently large time-scale differences between experiments and MD modeling, the elastic/yield response from the vastly different characteristics strain rates can be easily correlated. Their findings confirmed that an existing parameter set of the ReaxFF can be successfully used to predict the structure and elastic response of a cross-linked epoxy material.

The objective of this study is to establish the general applicability of the reactive force field in molecular dynamics to the modelling of thermo-mechanical behaviors of cross-linked epoxy materials. It will be demonstrated that the reactive force field can be used universally to capture mechanical properties as well as thermal response of cross-linked epoxy materials. To demonstrate this, a molecular model of EPON 862-DETDA epoxy system which can be generalized to other cross-linked systems as well was constructed and simulated to predict thermo-mechanical properties. The predictions are compared to experimental data in literature for the epoxy system.

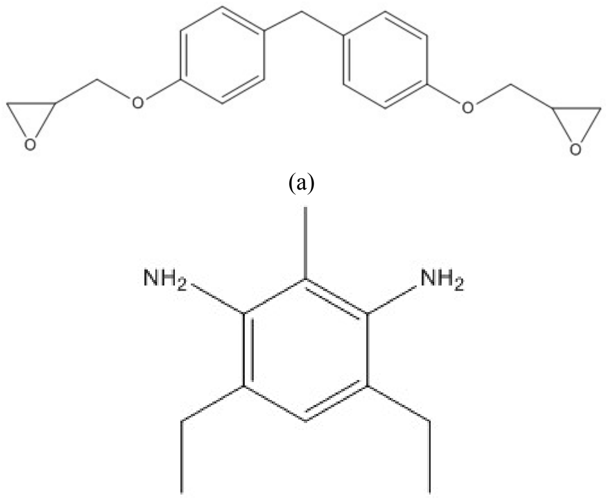
The paper is arranged as follows: Section 2 presents the methodology of the research work; Section 3 explains the results and discussion; Section 4 documents the conclusions.

2. Methodology

The detailed construction of the molecular model of the cross-linked epoxy is documented in this section. First, the modeling of uncrosslinked monomers i.e. epoxy resin, EPON 862 (diglycidyl ether of bisphenol-F) and the hardner, DETDA (diethylene toluene diamine). Second, the detailed crosslinking process and how the system is equilibrated before data sampling using LAMMPS (large-scale atomic/molecular massively parallel simulator) is described.

2.1 Structure of Resin and Cross Linker Molecule

Both EPON 862 (epoxy resin) and DETDA (hardner) monomers were constructed using BioChemDraw Ultra 14.0 package. The 3-D coordinates of the atoms that constitute both monomers, their bonds, angles and dihedrals topologies are established from the output of this package. Fig. 1 shows the molecules of EPON 862 and DETDA. First, based on the chemistry of reaction between the two molecules, a stoichiometry ratio of 2 molecules EPON 862 and a DETDA molecule was modelled. The molecules geometrical



(a)

(b)

Fig. 1 Molecular structure of (a) EPON-862 and (b) DETDA.

data as obtained from ChemBioDraw package is written into data file in LAMMPS format and the OPLS ALL atom force field [16-18] was utilized to establish the bond, angle, and dihedral parameters. In this force field, the total energy of the molecular system is the algebraic sum of all the individual energies of the bond, angle and dihedral; and 12-6 Lennard-Jones interactions. The non-bonded Van der Waals interactions were modeled with an interaction cutoff radius of 10 Å.

The constructed 2:1 molecular model was first modified as shown in Fig. 2 and this represents the pre-crosslinked configurations. Then, these structures were subjected to MD simulations using NVT (constant volume and temperature) ensemble at 300 K in order to relax the structures. Then, the model was minimized using the conjugate gradient stopping criterion in order to further reduce the internal forces. Thus reducing the internal residual stresses that were created from the initial construction of bonds, bond angles, and bond dihedrals. It should be noted that this process was done for 400 ps at a temperature of 300 K.

After the equilibrium configuration of the initial 2:1 stoichiometric structure, a stoichiometric mixture of 128 EPON-862 molecules and 64 DETDA molecules systems comprising 7488 atoms was built by replication in a periodic box. These initial simulations were performed using OPLS all atoms force field using LAMMPS molecular dynamics software as provided by Sandia National Laboratories. The replicated system was also equilibrated under NVT ensemble at 300 K and atmospheric pressure for 400 ps. The Noose-Hoover thermostat and barostat were used for temperature and pressure control, respectively. After which the system is relaxed, it was also minimized before the simulation box was compressed in stages under NVT ensemble with each stage done in quasi-equilibrium condition until a density of 1.2 g/cm^3 is achieved. It should be noted that at each stage of box reduction, one or two minimizations are performed on EPON 862-DETDA system to relax the coordinates of the atoms in the new volume of the simulation box. Once the final density is attained, the system was further minimized and equilibrated before cross-linking was performed as documented below.

2.2 Modelling and Crosslinking of Polymers

As mentioned in Ref. [14], it was important to initially create the model with a traditional fixed-bonding force field (OPLS) in order to efficiently establish the crosslinked structure. The OPLS allows “fix bond/create” command to be used to create the crosslink bonds for specified distances between atoms and reactive groups. However, this command could not be used with ReaxFF. It should be noted that the modified molecules of EPON 862 and DETDA as shown in Fig. 2 eliminate the initial hydration and activation process of crosslinking [1, 13]. The dot symbol attached to C and N shows the reactivity of methylene group in EPON 862 and active amine groups in DETDA, respectively toward crosslinking.

The crosslinking process is based on the active sites and it was performed under the NVT ensemble at a temperature of 300 K. The current approach for cross-linking assumes equal reactivity of primary and secondary amine. After the new bonds are formed, all

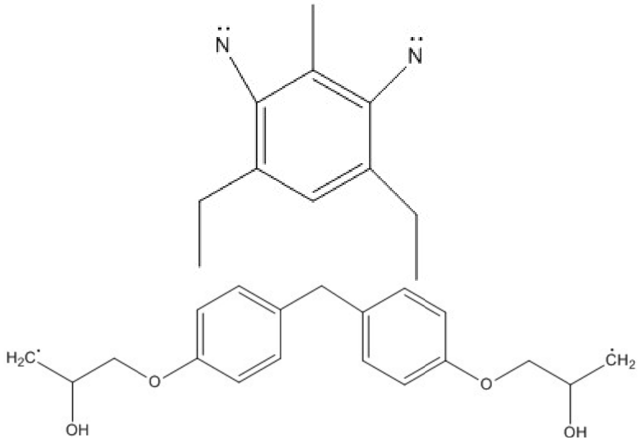


Fig. 2 Molecular structure of pre-crosslinked EPON 862 and DETDA monomers.

the new additional covalent terms (angles and dihedrals) are added to the connectivity definition. Since the chemical reactions are not directly considered in these simulations, bonding criteria are imposed to prevent unreasonable or unrealistic structural configurations and high levels of stress upon bond formation, which are unlikely to be adequately relaxed during energy minimization and molecular dynamic simulation. For this reason, a cut-off distance of 4.6 Å was chosen for crosslinking based on prior work [1] to achieve a cross-linking limit. The crosslink density was defined as the ratio of the total number of crosslinks that were formed to the maximum number of crosslinks that could be formed. It is important to note that for industrial grade epoxies, a broad range of crosslink densities of 60-95% is typically observed in experiments [19-23]. Therefore, the simulated crosslink densities were chosen to span part of this range. It should be noted that energy minimization and stress relaxations under NVT ensemble are implemented at regular intervals during this process of crosslinking. The cross-linked and equilibration structure of EPON 862 and DETDA system is as shown in Fig. 3. Three independent samples of equilibrated and cross-linked EPON 862/DETDA molecular dynamics models were established with OPLS.

After the initial process of cross-linking and relaxation process was brought into completion under the OPLS force field, the relevant information regarding the molecular configuration of the established structures (atom’s masses, coordinates, types, ID, and charge balance) which satisfies the requirements for ReaxFF were written into a new data file. Then, the system under the ReaxFF with the parameterizations of Liu et al. [24] was equilibrated in NVT. The temperature was increased during these simulations from 0.0 to 300 K for a period of 100 ps using a time step of 0.1 fs to ensure that the residual stress is taken out of the model. Then, the final equilibration of the system was done under NPT ensemble at 300 K for 100 ps using a time step of 0.1 fs and Nose-Hoover barostat and thermostat in order to obtain a fully relaxed structure.

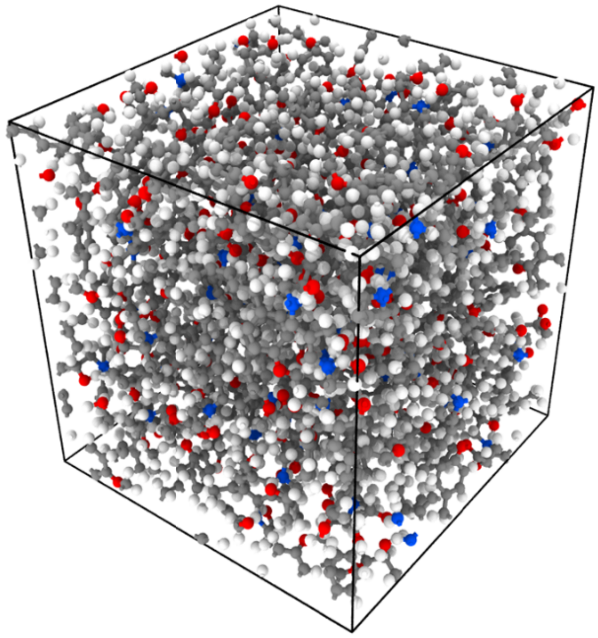


Fig. 3 Molecular structure of cross-linked and equilibrated structure.

On completion of the processes above, the sample was subjected to various forms of mechanical loadings in order to fully determine the mechanical behavior (Young’s modulus, bulk modulus, Poisson’s ratio and shear modulus, and yield strength) of the system. Also, to thermal loadings for the evaluation of thermal characteristics (glass transition temperature, volume shrinkage and thermal coefficient of expansion) of the system.

3. Results and Discussion

3.1 Elastic Constant

The elastic constants were calculated after the crosslinking and equilibration of EPON 862-DETDA system. Generally, geometric deformations were performed on the equilibrated structure in order to obtain the desired stress-strain relationship required for evaluation of the elastic constants. Specifically, each constant evaluated required peculiar type of deformation on the structure as documented below.

For the case of Young's modulus an axial strain is imposed on the periodic models using fix deform command in LAMMPS in NPH ensemble at one atmosphere and temperature of 300 K. This is to allow the Poisson's effect on two orthogonal directions. The corresponding stress component in the axial direction was determined for a complete stress strain response. The NPH simulations were run for 100 ps with time steps of 0.2 fs. The strain was applied incrementally at very time step in such a way that the desired strain magnitude was attained at the end of 100 ps. For each time, the overall Young's modulus of the model was calculated by

$$\sigma_{ii} = E\varepsilon_{ii} \tag{1}$$

where, ε_{ii} is the infinitesimal normal strain and σ_{ii} is the corresponding normal stress. The cumulative magnitude of the applied strain is ±0.006. A linear regression analysis was performed on the obtained data for the three models and the average was computed to obtain the Young's modulus as depicted in Table 1.

Furthermore, normal strains of the same magnitude were applied in three-orthogonal directions in the NVT ensemble at 300 K in order to obtain the dilatation and corresponding hydrostatic stress data required to compute the bulk modulus. The simulated methodology of spreading the strain magnitude equally over the time step throughout the entire simulation period of 100 ps is the same as given above.

For the volumetric strain the magnitude of the applied strains in all the three coordinate directions in both tension and compression is as given in Eq. (2).

$$\varepsilon_{xx} = \varepsilon_{yy} = \varepsilon_{zz} = \pm 0.006 \tag{2}$$

where, ε_{ii} is the infinitesimal normal strain tensor component with respect to coordinate direction i. Similarly, the dilatation for each time step of the MD model was calculated from

$$\Delta = \varepsilon_{xx} + \varepsilon_{yy} + \varepsilon_{zz} \tag{3}$$

While the corresponding hydrostatic stress is obtained from

$$\sigma_h = \frac{1}{3}(\sigma_{xx} + \sigma_{yy} + \sigma_{zz}) \tag{4}$$

where, σ_{ii} is the volume-averaged viral stress tensor component with respect to the coordinate direction i. The simulated dilatation and the corresponding hydrostatic stress for each time step were used to perform linear regression according to Eq. (5) to obtain bulk modulus.

$$K = \frac{\sigma_h}{\Delta} \tag{5}$$

It should be noted that the bulk moduli calculated for the three independent models were averaged and presented in Table 1.

The present results as depicted in Table 1 showed a good agreement with simulated results in literature. Also, Fig. 4 shows the average value of the predicted result and experimental data [9] as a function of strain rate. This figure is important since Young's modulus of thermosetting polymers is generally dependent on applied strain rate. Considering the fact that the

Table 1 Elastic properties of cross-linked structures.

Property (GPa)	E (Young's mod.)	G (shear mod.)	K (bulk mod.)	v (Poisson's ratio)
Present 85% cross-linking	5.252	1.785	5.27	0.3478
Li et al. [2]	3.2-3.5	-	-	0.43-0.47
Wu and Xu [8]	5.198	1.924	5.804	0.3507

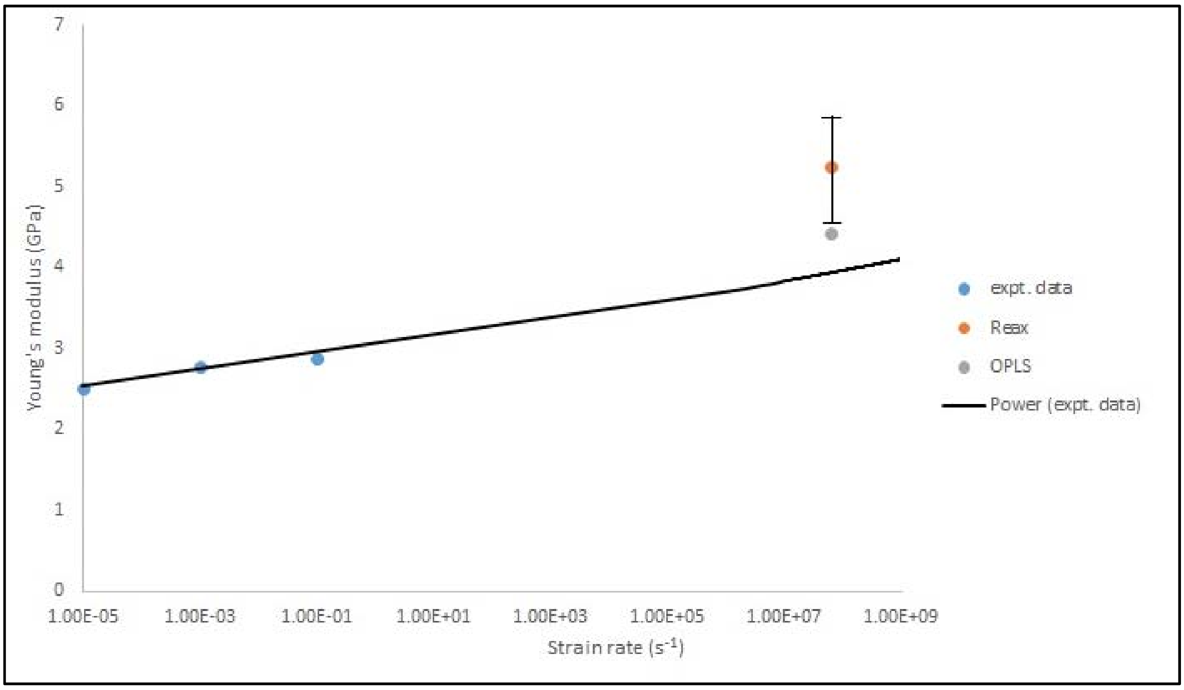


Fig. 4 Predicted and measured Young's modulus vs strain rate. The superposed line indicates the trend of the experimental values.

simulated deformations are at relatively high strain rate, the line that represents experimental data was superposed to allow the comparison of the present simulated result with both experiment and reference [13] where OPLS force field was utilized. The line is a power law least-square fit of the experimental data points. As expected, the experimental values for the Young's modulus are less than the estimated results obtained from both force fields. However, looking at the experimental trend in modulus with strain rate, the range and trends of experimental values agree well with both computational values. It should be noted from Fig. 4 that the computational value obtained from ReaFF is higher than that obtained from OPLS. This may be attributed to the fact that charge balance on the individual atom is maintained in Reactive force field.

It is noteworthy that typical computational MD-based model that predicts elastic properties of polymers typically ignores the effect of simulated strain rate, even though the influence of strain rates has been explicitly documented [25]. The reason for this omission might be that the Young's moduli of polymers for a large range of strain rates are on the same order of magnitude as shown in Fig. 4 and the simulation of laboratory strain rates is nearly impractical to achieve for fully atomistic models. Odegar et al. [14] asserted that the various differences between predicted and experimentally-determined values of modulus are sometimes justified by statistical scatter in the predicted modulus values from different simulated samples [26]. However, it is demonstrated in Fig. 4 that the predictions in modulus can agree with experiments when the strain rate discrepancy is carefully considered.

The shear modulus was determined using a triclic box having periodic boundary condition. A three-dimensional shear strain was applied to the EPON 82-DETDA molecular models as given in Eq. (6).

$$\gamma_{xy} = \gamma_{yz} = \gamma_{zx} = \pm 0.015 \qquad (6)$$

where, γ_{ij} is the infinitesimal engineering shear strain component with respect to the i and j coordinate directions. The corresponding shear stress components τ_{xy}, τ_{yz} and τ_{zx} were calculated for each time step. It is noteworthy to mention that this simulation was performed in NVT ensemble at 300 K. A linear regression analysis was performed on the simulated stress-strain to determine the shear modulus based on Eq. (7) for the three independent models.

$$\tau_{xy} = G\gamma_{xy} \tag{7}$$

The obtained shear modulus as simulated in this model is as given in Table 1 in comparison to the results found in the literature. Also, the response of EPON 862/DETDA system to shear deformation is shown in Fig. 5. The resulting average values of the simulated shear deformations and those obtained experimentally [9] at three lower shear strain rates are compared in this figure. Similarly, the line shown in this figure is a power law least-squares fit of the experimental data points. Due to higher simulated strain rate, the predicted shear modulus is higher than experimental values. However, with due consideration to the experimental trend in modulus with shear strain rate, the range and trends of predicted values agree very well with the experimental data. As can be seen in Fig. 5, the shear moduli of polymers for a wide range of shear strain rates are on the same order. This perhaps explains why MD-based predictions of elastic properties of polymers typically ignore the influence of simulated strain rate.

In this study, Poisson's ratio was calculated from Eq. (8) below using the obtained value of shear and bulk moduli. The calculated value of Poisson's ratio is shown as shown in Table 1.

$$\nu = {3K - 2G}/{2(3K + G)} \tag{8}$$

Also, the sample was subjected to tensile deformations in x-, y-, and z- directions, respectively at a strain rate of 2 × 10^8/s under NPH ensemble with barostat and thermostat control. This is to allow Poisson's effect in the two lateral directions. The deformation was done at a temperature of 300 K and a pressure of 1 atmosphere until 20% axial (~18% true strain) is reached. Using a time step of 0.1 fs, the deformations were applied gradually for 1,000 ps. Poisson's ratio was determined by finding the negative slope of the lateral/longitudinal strain curve up to yield point. As shown in Fig. 6, the average lateral strain values obtained from the two transverse strains of the simulation box exhibited a slight scatter and a decreasing value with increased longitudinal strain. It is important to note that this scatter is a function of

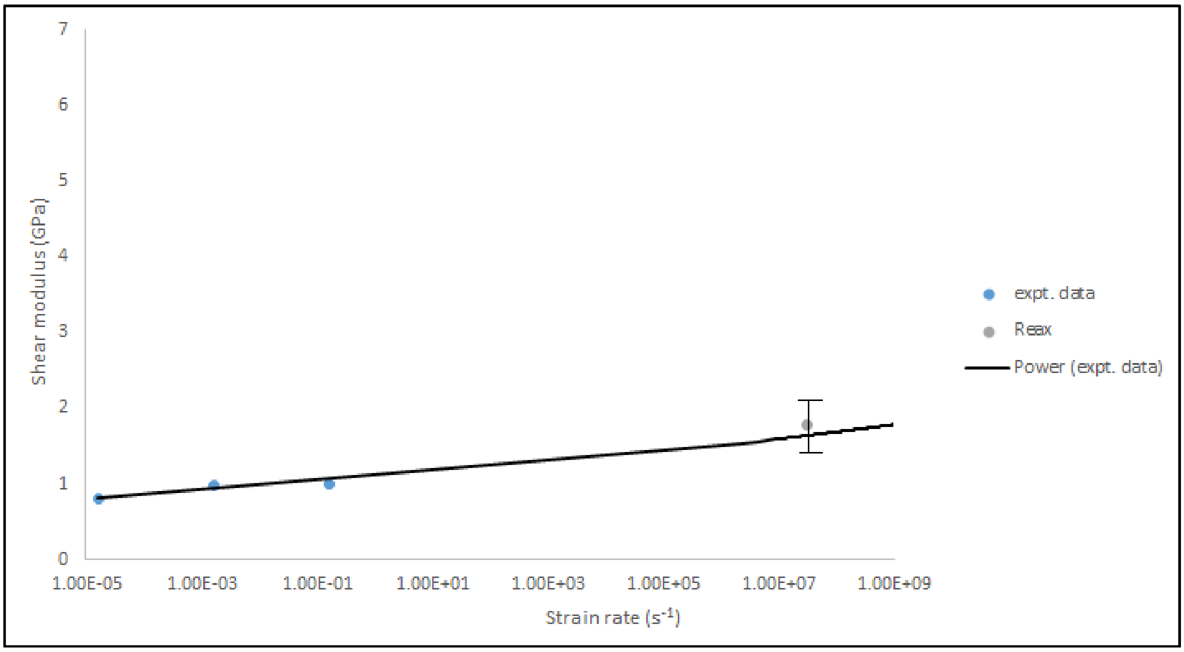


Fig. 5 Predicted and measured shear modulus vs. strain rate. The superposed line indicates the trend of the experimental values.

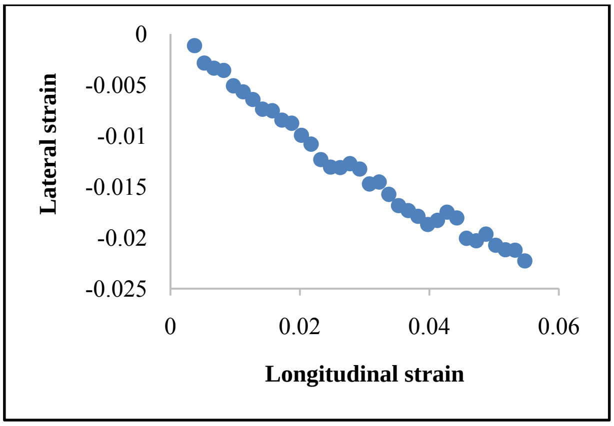


Fig. 6 The plot of lateral strain vs. longitudinal strain from MD simulations.

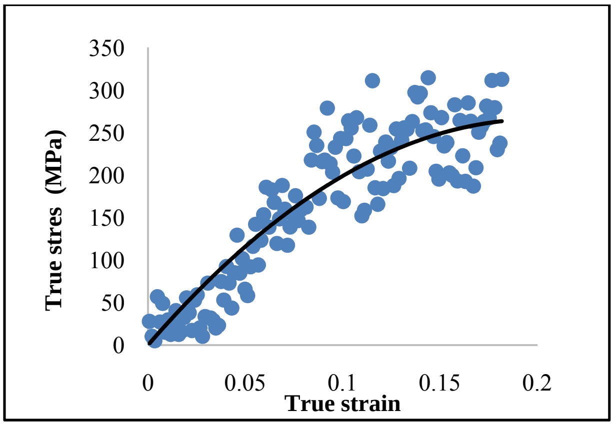


Fig. 7 The stress strain-curve for EPON 862/DETDA using ReaxFF.

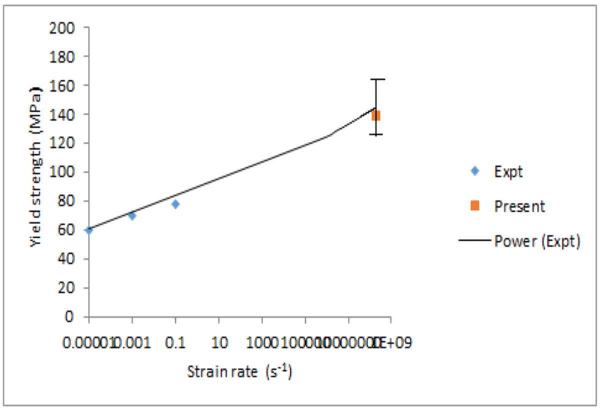


Fig. 8 The estimated and measured yield strength vs. strain rate.

compressibility of the material and system size. The estimated Poisson's ratio from this simulation was 0.3983 for a strain rate of 2 × 10^8 s^{-1}. This confirmed that both results obtained from Eq. (8) and the plot in Fig. 6 showed a very good agreement.

The yield strength of the EPON 862/DETDA system is obtained from the stress-strain plot in Fig. 7. The yield strength is defined as the point where the straight line drawn from 0.2% strain (ε = 0.002) parallel to the elastic portion of the stress-strain curve intercepts the curve. The average value of the predicted yield stress from this simulation is 138.4 MPa. This simulated value as compared with experimental data [9] is shown in Fig. 8. As in Figs. 4 and 5, a power-law least-squares fit of the experimental data is shown in Fig. 8. It can be seen from this figure that there is a very good agreement between predicted and measure values of yield stress when strain rate effect is considered. It should be noted that the superposed line indicates the trend of the experimental values.

3.2 Glass Transition Temperature

In order to study the temperature dependence of various thermodynamic quantities, a slow heating process followed by an annealing simulation was performed. That is, the system was first heated from 300 K to 600 K under an NPT ensemble for 50 ps in 1 atmosphere and then slowly cooled down at the rate of 3 K/5 ps from 600 K to 300 K under atmospheric pressure which was controlled by a Noose-Hoover thermostat and barostat.

The change in density as a function of temperature is plotted in Fig. 9. The density at room temperature is within the neighborhood of 1.16 g/cm^3 and is in good agreement with simulated result [1] that was determined to be 1.2 g/cm^3 on similar system. A kink in the density against the temperature curve is observed in Fig. 9. The kink is usually identified as transition temperature (T_g). It can be seen in this case that it occurs around 175 °C. The T_g value is usually controlled by cooling rate as well as method of measurement [1]. Bandyopadhyyay et al. [26] predicted a T_g of 151.2 °C for 76% cross-linked structure and Varshney et al. [1] predicted a T_g of 105 °C for the same EPON 862-DETDA system but

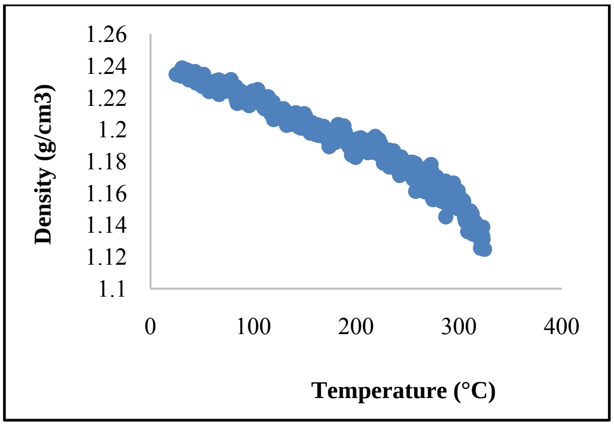


Fig. 9 Density variation as a function of temperature for ReaxFF.

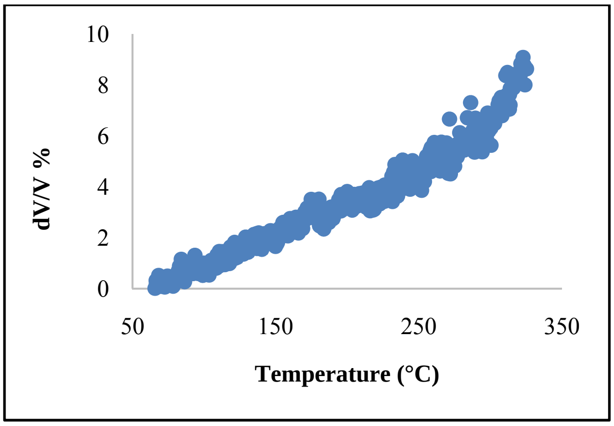


Fig. 10 Fractional volume change as a function of temperature for ReaxFF.

with a crosslink density of 95%. Miller et al. [27] experimentally measure a T_g of 150 ºC for the same system, though the actual density is unknown. Aluko et al. [13] utilized OPLS force field and estimated a T_g of 142 ºC. Hence, the predicted T_g using ReaxFF is slightly higher than when OPLS was used.

3.3 Coefficient of Thermal Expansion

Similarly the simulated heating and cooling process as described above was used to determine the rate of volume shrinkage of EPON 862-DETDA system with temperature. Coefficient of thermal expansion is also an important thermodynamic property in composite materials since they are used at different temperatures in engineering applications. The CVTE (coefficient of volume thermal expansion), α, is defined as

$$\alpha = \frac{1}{V_o}\left(\frac{\partial V}{\partial T}\right)_P \qquad (9)$$

where, P, T and V_o are pressure, temperature, and initial volume of the system, respectively. For isotropic materials, the CLTE (coefficient of linear thermal expansion), β, is given as

$$\beta = \frac{\alpha}{3} \qquad (10)$$

The fractional volume shrinkage (dV/V_o) versus temperature is depicted in Fig. 10, and as expected a kink suggestive of the T_g is observed with the neighborhood of 175 °C. Furthermore, the slope of the curve is defined as CVTE, α. Applying Eq. (10) to the slope of the curve above and below glass transition temperature, the calculated values of CLTE both above and below glass transition temperatures were obtained as 42.9 × 10^{-5} (°C^{-1}) and 24.6 × 10^{-5} (°C^{-1}), respectively. These results in comparison with ones reported by Fan et al. [5], Aluko et al. [13], and Wang et al.'s experimental findings [28] are as shown in Table 2.

Table 2 The coefficient of linear thermal expansion of cross-linked structures.

αx(10^{-5} (°C^{-1})	ReaxFF	OPLS [13]	Fan et al. [5]	Wang et al. [28]
Above T_g	42.9	17.4	18.5	18
Below T_g	24.6	11.9	5.5	6.4
% cross-linking	85	85	100	-

4. Conclusions

The reactive force field of Liu was utilized to perform the molecular dynamics of EPON 862/DETDA system with the objective of predicting its thermo-mechanical properties. The results showed that ReaxFF with Liu parameter set is an excellent tool for predicting mechanical response as well as thermal behavior of EPON/DETDA system. Unlike the traditional fixed-bonding force fields, the generality of the reactive force field makes it applicable to MD in order to gain more insight into the behavior of more advanced and epoxy-based network systems. It was also demonstrated in this study that the predicted results comprising the thermal properties (glass transition temperature, volume shrinkage and thermal coefficient of expansion) and mechanical properties (Young's modulus, bulk modulus, Poisson's ratio and shear modulus and yield strength) are generally in good agreement with both experimental data as well as computational results found in literature.

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