MOLECULAR DYNAMIC SIMULATION AND EXPERIMENTAL INVESTIGATION OF SHORT GLASS FIBER REINFORCED POLYMERIC NANOCOMPOSITES FOR MECHANICAL PROPERTIES

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ABSTRACT

Epoxy material reinforced with nanomaterial have recently received attention in both scientific and industrial communities due to their enhanced mechanical properties for structural application. The study of these materials is still empirical in nature and a finer degree of control of their properties is needed. Molecular dynamics (MD) simulation is one of the most effective way of mechanical property evaluation of these material without carrying out expensive and time-consuming experimentation work. In this paper, MD simulation of diglycidyl ether of bisphenol F(DGEBF) and diethyl toluene diamine (DETDA), a resin and hardener mixture reinforced with multiscale reinforcement. Chopped E glass fiber is carried to study their reaction kinetics so that molecular level reason for the property improvement can be identified. Study shows that uniform isotropic properties can be achieved by this type of multiscale reinforcement. Molecular dynamics simulation of neat epoxy was carried out which shows that maximum tensile strength up to 100MPa.The obtained structure in MD simulation had 55% crosslinking with around 220 new bond formation between the resin and crosslinking agent. The density obtained by this simulation was 0.77gm/cc which will go on increasing as crosslinking goes on increasing. Tensile strength obtained by MD simulation is compared with the experimental result of 55MPa difference observed may be because of the highly stressed structure of the generic resin obtained from the supplier and standard data of curing cycle was available.

Keywords: Chopped E-Glass fiber, Molecular Dynamic Simulation, Resin Testing,

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INTRODUCTION

A small amount of chopped E-glass fibers reinforced in epoxy resin is an ideal combination to understand and analyze the stress transfer mechanism from fiber/matrix interface in polymeric composites. Higher fiber content may lead to problems such as gas entrapment in fibers due to degassing of resins during the curing process, improper wetting of fibers, etc. These effects may mislead the understanding of stress transfer mechanism from resin to fiber when mechanical characterization of such polymeric composites will be done [2]. These epoxy resins with nanometric reinforcement such as carbon nanotubes (CNTs) have got attention in research communities due to enhancement in mechanical properties [3]. These properties enhancement

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attributed to the high surface to volume ratio of CNTs which increases the contact area between the resin and CNTs. However, from the experimental point of view, it is very difficult to characterize these materials and to manipulate the fabrication process. The development of such materials is empirical in nature and a finer degree of control of their properties cannot be achieved so far. Molecular dynamic (MD) simulation is one of the ways where there is no need to perform these time-consuming and costly experiments and which reveals the reasons of property improvement at molecular level. Among several types of thermoset resins, diglycidyl ether of bisphenol-F (DGEB-F) is known to be very compatible with modern lightweight structures for aerospace and automobile applications. Findings in the literature indicate that the use of nano-fillers and conventional microscale fibers as multiscale reinforcements, significantly improve the overall properties of composites. The focus of current study was to use very small amount of randomly oriented chopped E-glass fibers. The weight percentage variation considered were 1%, 2%, and 3% with the nominal diameter of 13 - 17microns and length not more than 6mm. The fibres were reinforced with DGEB-F resin and hardener DETDA to form a composite. Significant improvement in mechanical properties of composite were observed with the sonication of fibers in the resin. The mechanical testing results shows nearly isotropic properties can be achieved for these types of composites. With addition of nanomaterial in the resin further improvement of mechanical properties can be achieved. Molecular dynamics simulation of neat resin revealed that a very high degree of crosslinking could be one of the reasons for the nearly isotropic properties of the material system under consideration [4].

EXPERIMENTATION

2.1 Material System

Neat epoxy Epofine-281 DGEBF, Finehard-5200 DETDA a hardener were supplied by Finefinish, India. The resin and hardener density were 1190 kg/m^3, 1000 kg/m^3 respectively. The resin to hardener weight fraction ratio was 73.6:26.4. This resin was used due to its high wettability, good balance of mechanical, adhesive, chemical, and electrical properties, and superior physical properties. Chopped E-glass fibers were purchased from Arrow Technical Textile Pvt. Limited, India with an average length of 6 mm, and diameter between 13-17 microns. These glass fibers were chosen because they were widely used for structural applications, ease of handling, quick wet out, and have compatibility with the resin system.

2.2 Fabrication Process

Four composite panels of size 0.3048 m x 0.3048 m were fabricated. One was without chopped E-glass fiber and three with chopped E- glass fibers of varying weight fractions. Chopped E-glass fibers of 1% of the total weight of resin and hardener system were mixed with resin. The mixture was sonicated for 120 minutes. On-time and off time for sonication was set to 5 seconds. The maximum temperature of the mixture during the sonication process that could reach was set to 65^{0}C with 50% of the maximum power of the sonicator. Sonicated mixture was then added with hardener and mixed manually. For degassing and to supply the activation energy to this mixture, it was heated up to 45^{0}C and steering after every 5 minutes. This process was continued for the next 30 minutes. The mixture was directly poured in steel mould with a release agent applied over it. Mould was kept in the furnace with a ramp rate of 2^{0}C /min till it reaches 120 ^{0}C and the soak time was 4 hours. The Sample was allowed to cool in the furnace

for next 12 hours. A similar procedure was adopted for 2% and 3% chopped E-glass fiber/epoxy panel preparation. After curing, visual inspection of the three composite panels was carried out and found free from voids and defects.

Figure 1: Sonication Process

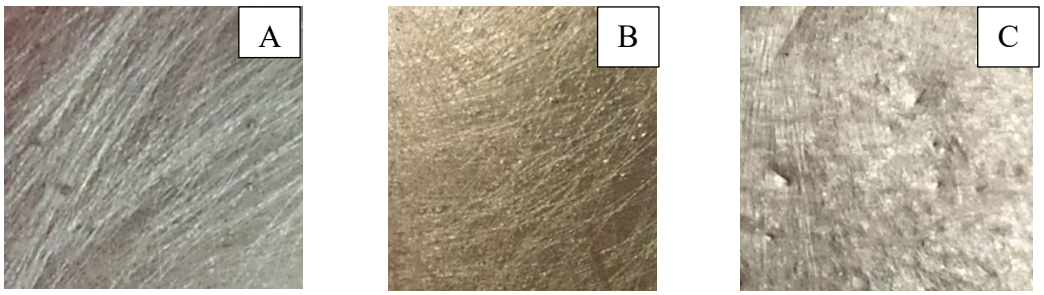

Figure 2: Microscopic Image of A)1%, B)2%, C)3% Chopped E-Glass Fiber Panels

2.3 Tensile Testing

Tensile tests were carried out as per ASTM D638 standard with a crosshead speed of 2 mm/s at room temperature. Since the weight fraction of fiber was very low compared to the resin this standard was taken for testing. The specimens were cut using a water jet machine. The test was performed on Shimadzu AGS-X 100KN.

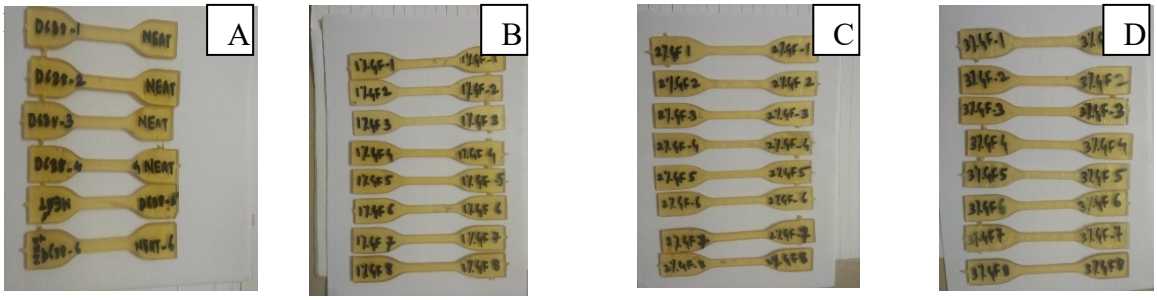

Figure 2: Tensile Test Specimen as per ASTM D638 for a) neat resin, b) 1% c) 2%, d)3% chopped E-glass fiber/epoxy composites

For calculation of passion's ratio one sample from each was tested with strain gauges and data is collected by using KYOWA data acquisition system, Japan installed on the Shimadzu 100kN UTM .

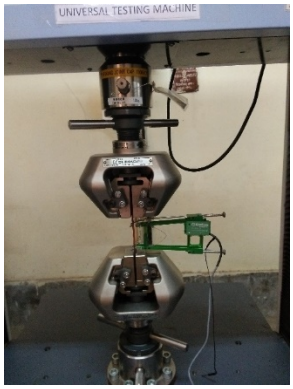

Figure 3: Tensile Test

From the test data, tensile modulus and strength were determined as per the ASTM standard [5].

Table I: Tensile Properties of Neat, 1%, 2%, 3% chopped E- glass fiber and DGEBF/DETDA

Sample	Young's Modulus (N/mm^2)	Maximum Tensile Strength (N/mm^2)	Percentage Increase in tensile Strength	Percentage Increase in Modulus	Poisson's Ratio
DGEBF +DETDA	3211.26	45.41	N.A.	N.A.	0.50
1% C-GF + DGEBF +DETDA	3509.45	52.32	15.21%	15.68%	0.50
2 % C-GF + DGEBF +DETDA	3715.10	48.34	6.45%	15.70%	0.49
3% C-GF +DGEBF +DETDA	3811.28	52.08	14.68%	18.68%	0.49

MOLECULAR MODELLING AND ANALYSIS

The macro-level material mechanical properties depend on the interactions at the fundamental molecular level of the constituent materials. The cured molecular models of epoxy consisting DGEBF and DETDA were developed using Cognac reaction Module in J-OCTA 4.2 (JSOL Corporation Japan) development tool. The molecular models were configured for various degrees of networking of the cross-linked structure. The parameters were set using Dreiding force field parameters to establish the bond, angle, and dihedral parameters [6]. Simulations carried out in NPT thermodynamic state (constant number of atoms, pressure, and temperature) and Velocity Verlet algorithm numerical scheme used for the dynamic analysis.

2.4 Molecular Modeling of Material Constituents

Monomer models were prepared by using COGNAC monomer modeler. DGEBF has an epoxy end chain (diepoxy) with bisphenol-F inner organic group. This epoxy structure is highly amorphous with very susceptibility for crosslinking polymer to form a thermoset polymeric compound. The di-epoxy ends provide the potential for polymerization cure by cross-linking reaction. Figure 4 shows the molecular/ chemical structure of the epoxy model. The molecular weight of epoxy is 314.222amu.

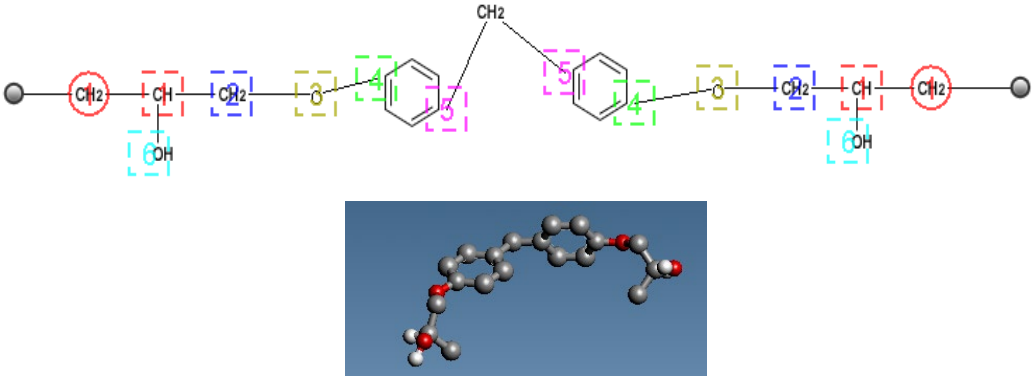

Figure 4: Molecular/ Chemical Structure of the epoxy model

The curing agent used in the processing was DETDA, which was an aromatic polyamine an amorphous organic compound. The end di-amine chain serves as a crosslinker in a complex polymeric structure. It has ability to give off its hydrogen to the epoxy molecule to form a hydroxyl group and bond to the carbon atom in the epoxy ends. Molecular weight DETDA is 174.218 amu. Figure 5 shows the molecular structure for DETDA.

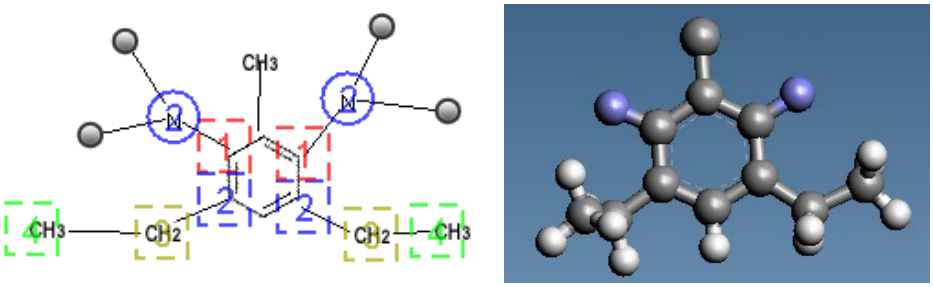

Figure 5: Molecular Structure for DETDA

During monomer modeling reaction sites were generated for DGEBF at the carboxyl group and DETDA four reaction sites were generated by removing hydrogen and placing No-hydrogen at two amines groups as shown in figure 4 and figure 5. Molecular mechanics (MM) calculations were carried out to analyze the stereochemical conformation of a molecular system with a particular arrangement of atoms using the potential energy surface. The potential energy surface is calculated by a set of parameters and potential functions (also known as 'force field'). The MM method is especially useful for the study of equilibrium geometry of systems.

The reaction model was developed by taking 150 molecules of DGEBF and 75 molecules DETDA so that the mixing ratio of 73.6:26.4 can be achieved. Simulation conditions were set in such a way that if two atoms come in the vicinity of $4A^0$ they will form a bond. Using a stoichiometric ratio of 1:1 to concur with the mixing ratio during processing, the molecular unit consisting of 2, 3, and 5 molecules of epoxy and curing agent were developed.

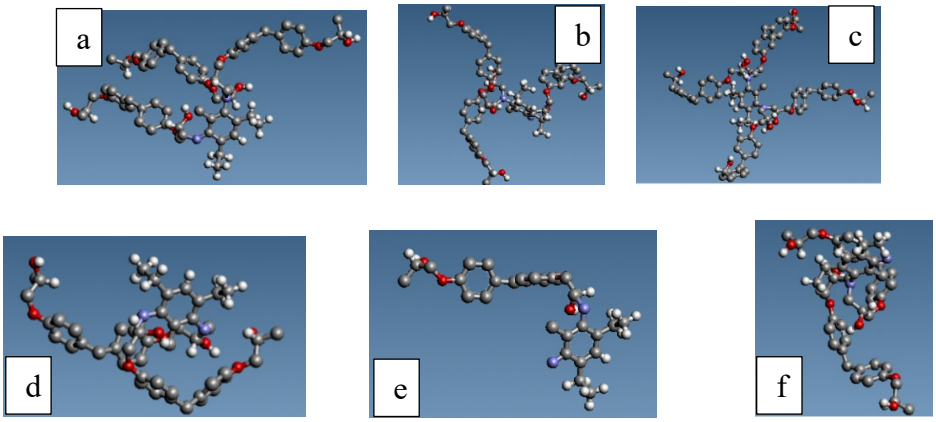

Figure 6: Pre-reaction molecular unit development consisting of 2, 3 and 5 molecules of epoxy and curing agent a)1 Amine -3 DGEBF b) 1 Amine -3 DGEBF another orientation, c) 1 Amine -4DGEBF d) 1 Amine -2DGEBF, e) 1 Amine -1DGEBF, and f) 1 Amine -2 DGEBF another orientation

2.5 Molecular Dynamics Simulation

The simulation input file was generated by applying periodic boundary conditions in all three directions and the cell size taken was 43.67 x 43.67 x 43.67 A^0. The expected density was set to 1.2gm/cm^3. NVE (constant number of molecule, constant volume, and constant energy) ensemble is applied. Temperature is kept at 300K, the time interval was taken as 30 fs. First, few MD simulations are carried out for achieving energy minimization. The same structure is used for the multiple numbers' MD simulation so that the expected density will be achieved. NPT_Anderson_Noose_Hoover thermostat is used to keep temperature and pressure constant, with a time step of 1fs with dynamic relaxation and 10000 steps with a cut-off distance of $4A^0$. Relaxation simulation was carried out under NVE by reducing the size of the simulation box until it will reach to a density of 1.2gm/cc.

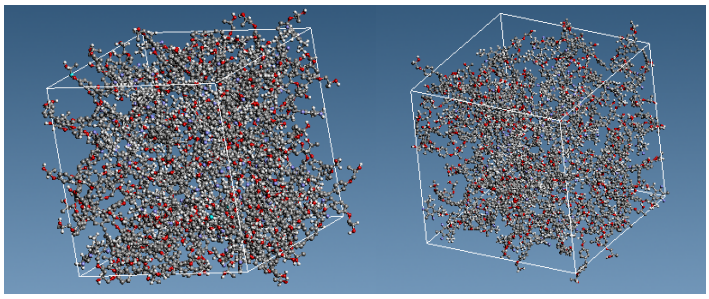

Figure 7: Initial RVE before crosslinking and after crosslinking structure of DGEBF and DETDA

RESULT AND DISCUSSION

The tensile properties of DGEBF/DETDA epoxy was significantly improved with the addition of a very small percentage of randomly oriented chopped E-glass fibers. Tensile test of neat, 1%, 2%, and 3% chopped glass fiber composite was carried out as per ASTM D638 standard. The tensile strength for neat, 1%, 2%, and 3% chopped E-glass fiber composites were observed to be $45.41N/mm^2$, $52.32N/mm^2$, $48.34N/mm^2$, and $52.08N/mm^2$ respectively withcorresponding standard deviation values of 0.1224, 0.0179, 2.34, and 2.176. The standard deviation value goes on increasing above 3% since it was difficult to achieve even dispersion of fibers in the epoxy. In 1%, 2%, 3% by weight sample, tensile strength is observed to be increased by almost 15.21%, 6.45%, and 14.68% compared with neat epoxy resin. The tensile modulus increased by 15.68, 15.70 %, and 18.68%. It was also observed that due to sonication even dispersion of fibers in random orientation can be possible only up to 3%. There was staking of fibers was going to happen if the percentage of fibers increases beyond 3% and uneven properties in different directions. The entire mixture is difficult to pore if the percentage of fiber goes on increasing in the mould and there was a possibility of air entrapment in the panels due to staking of fibers. Poission's ratio of all samples is observed near 0.49 which can be concluded that nearly isotropic properties can be achieved by this method of sample preparation. With the addition of SWCNT further significant improvement in mechanical properties can be possible with the same methodology [7].

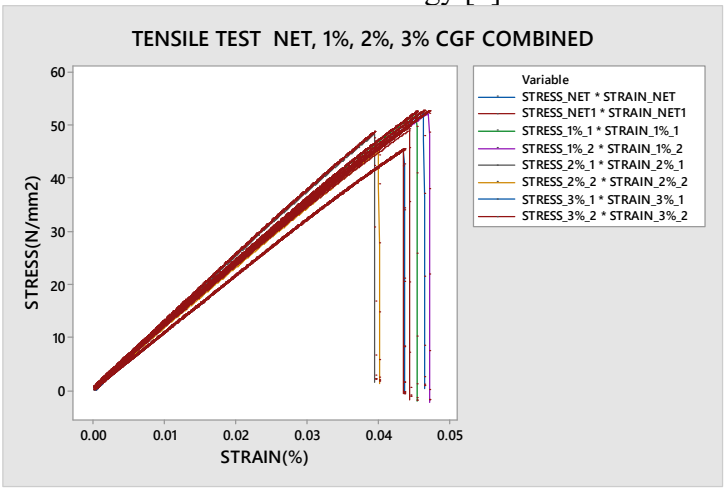

Figure 8a: Stress verses strain graph for neat, 1%, 2%, and 3% chopped E-glass fiber in chopped E-glass fiber/epoxy composites

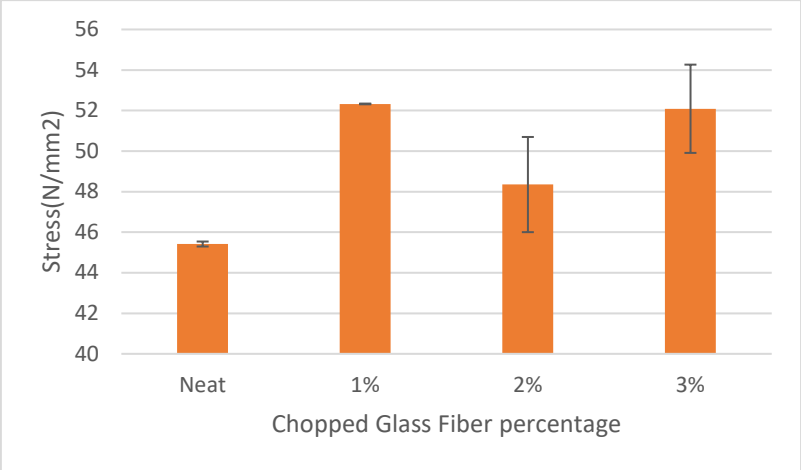

Figure 8b: Comparison of Tensile strength verses weight percentage of chopped E-glass fiber in chopped E-glass fiber/epoxy composites

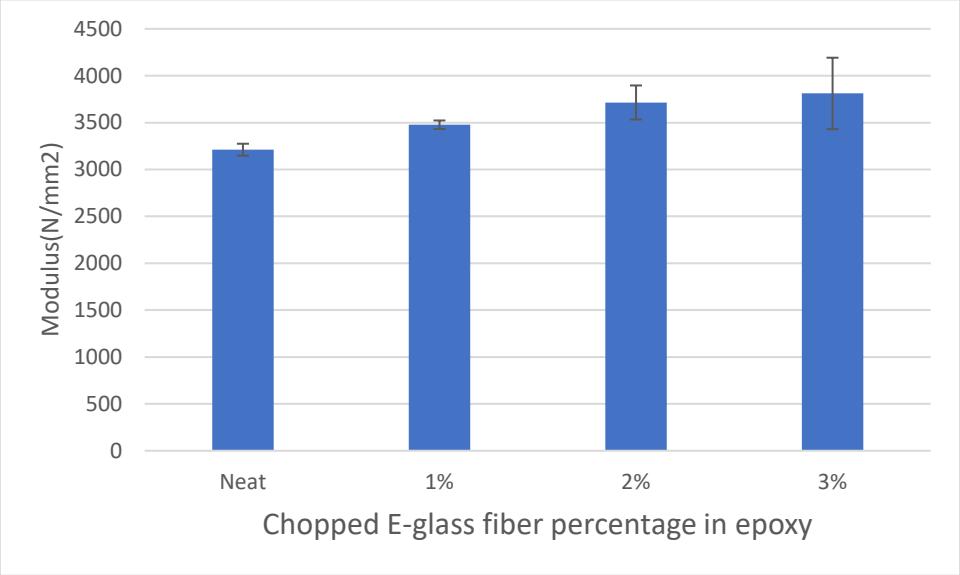

Figure 9: Comparison of Tensile Modulus verses weight percentage of chopped E-glass fiber in chopped E- glass fiber/epoxy composite

Molecular dynamics results show that the four reaction sites on the crosslinking agent lead to formation of highly complex network structure with crosslinking density upto 90% can be achieved.

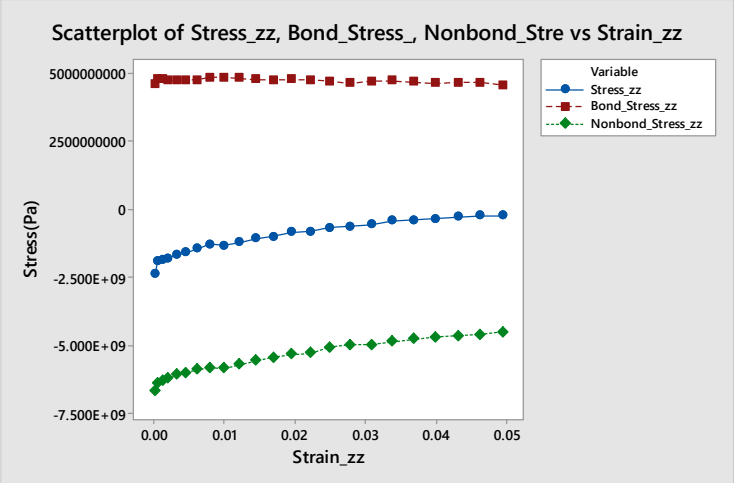

Figure 9: Stress verses Strain for Stress-zz, bonded and nonbonded interaction obtained form Molecular Dynamics simulation of DGEBF/ DETDA

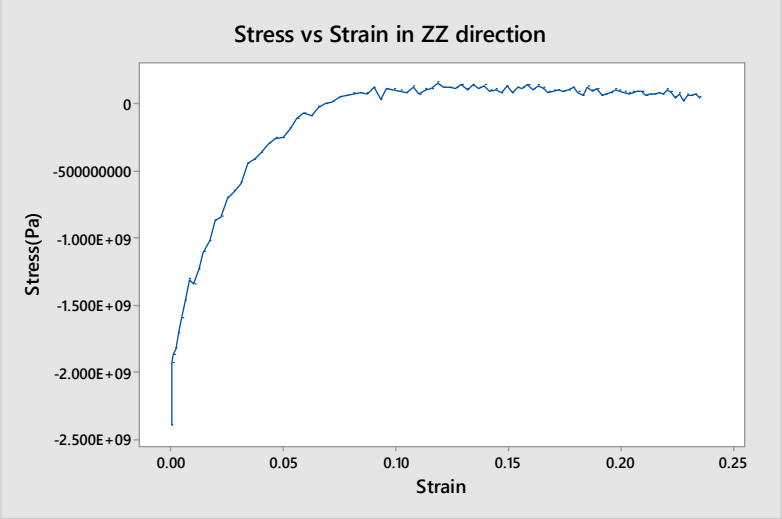

Figure 9: Stress vs Strain in zz, Direction

Maximum Stress in ZZ direction of RVE is around 100MPa of 150molecule of DGEBF and 75 molecules of DETDA. The difference in the experimental and MD simulation is 55MPa this higher stresses may be because of small number of molecules taken into consideration for mimic the actual curing of epoxy and fully cross-linking of the matrix.

5. CONCLUSION

In the present study, mechanical properties such as tensile strength and tensile modulus of neat epoxy resin Epofine-281, Finehard-5200 crosslinking agent with chopped glass fibers with 1%, 2%, and 3% were compared. The Sonication process was used to ensure uniform distribution of fibers in resin. It was observed that 1% fiber tensile strength was improved by almost 15% attributed to complete wettability of fibers as the percentage increases dry fibers were observed in the samples. Tensile modulus goes on increasing as the percentage of fiber goes on increasing. As the fiber percentage increases the air entrapment also goes on increasing which will lead to anisotropic behavior of the samples test specimens. Molecular dynamics simulation of neat epoxy was carried out which shows that maximum tensile strength up to 100MPa.The obtained structure in MD simulation had 55% crosslinking with around 220 new bond formation between the resin and crosslinking agent. The density obtained by this simulation was 0.77gm/cc which will go on increasing as crosslinking goes on increasing. Tensile strength obtained by MD simulation is compared with the experimental result of 55MPa difference observed may be because of the highly stressed structure of the generic resin obtained from the supplier and standard data of curing cycle was available. In further experimentation, if we incorporate the SWCNT in resin with a very small percentage dramatic improvement in mechanical properties can be obtained as per the available present literature.

REFERENCES

[1] Ananyo Bandyopadhyay, Benjamin D. Jensen, ´ Atomistic Modeling of Cross-linked Epoxy Polymer', 51st AIAA/ASME/ASCE/AHS/ASC Structures, Structural Dynamics, and Materials Conference, 12 - 15 April 2010, Orlando, Florida.

[2] 'Comparison of mechanical properties of EPON 862/W with and without TEOS electrospun nanofibers in nanocomposite', DK Shinde, L Emmanwori, AD Kelkar - SAMPE Seattle 2014, pg. 59-4040, June 2, 2014

[3] Sheikhnejad O, Nakamoto T, Kalteis A, Rajabtabar A, Major Z,Molecular Dynamic Simulation of Carbon Nanotube Reinforced Nanocomposites: The Effect of Interface Interaction on Mechanical Properties. MOJ Poly Sci 2(1): 00038. DOI: 10.15406/mojps.2018.02.00038
[4] Park H, Kim B, Choi J, Cho M, Influences of the molecular structures of curing agents on the inelastic-deformation mechanisms in highly-crosslinked epoxy polymers, Polymer (2018), doi: 10.1016/j.polymer.2017.12.055.
[5] ASTM D 638, "Standard test method for tensile properties of plastics," ASTM International, USA
[6] Mayo, Stephen L. and Olafson, Barry D. and Goddard, William A., III (1990) DREIDING: A generic force field for molecular simulations. Journal of Physical Chemistry, 94 (26). pp. 8897-8909. ISSN 0022-3654.
[7] "Carbon nanotubes as reinforcement in composites: A review of the analytical, numerical and experimental approaches", Sadegh Imani Yengejeh, Seyedeh Alieh Kazemi, Andreas, Computational Materials Science, 2017 http://dx.doi.org/10.1016/j.commatsci.2017.04.023 0