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MULTISCALE MODELING: THERMAL CONDUCTIVITY OF GRAPHENE/CYCLOALIPHATIC EPOXY COMPOSITES

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MULTISCALE MODELING: THERMAL CONDUCTIVITY OF
GRAPHENE/CYCLOALIPHATIC EPOXY COMPOSITES

By

Sorayot Chinkanjanarot

A DISSERTATION

Submitted in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

In Mechanical Engineering-Engineering Mechanics

MICHIGAN TECHNOLOGICAL UNIVERSITY

2017

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This dissertation has been approved in partial fulfillment of the requirements for the Degree of DOCTOR OF PHILOSOPHY in Mechanical Engineering-Engineering Mechanics.

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PREFACE

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ABSTRACT

The thermal property of epoxy as the binder in the Carbon Fiber (CF) composites, especially thermal conductivity is important to achieve the advance technology and to improve the performance of materials. Multiscale modeling including molecular dynamic (MD) modeling and micromechanical modeling is used to study the properties of neat Cycloaliphatic Epoxies (CE) and Graphene nanoplatelet (GNP)/CE with and without covalent functionalization.

The thermal properties (glass-transition temperature, thermal expansion coefficient, and thermal conductivity) and mechanical properties of CE system are investigated by MD modeling using OPLS-All Atom force field. A unique crosslinking technique is developed to achieve the cured CE models which has the complex curing mechanism. The thermal conductivity and elastic modulus of CF/CE models are further calculated by using micromechanical modeling. The results are validated with the experiments which are in good agreement.

GNP/CE nanocomposites models are established by MD with four different levels of GNP dispersion, namely, 1, 2, 3, and 4 layer(s) of graphene. The thermal conductivities of GNP/CE nanocomposites models are determined by Equilibrium MD (EMD) method. The thermal conductivities are randomized by arithmetic average and varied GNP volume fractions using micromechanics. The resultant thermal conductivities increase with the GNP volume fraction and the better dispersion which compared well with experiments. The 1-layered GNP/CE (perfectly dispersed) model gives the highest thermal conductivity.

The covalently functionalized GNP (fGNP)/CE models are created by functionalizing carboxyl groups onto the single-layered GNP surfaces by MD modeling. The similar method for the pristine GNP/CE models is applied to obtain the effective thermal conductivities fGNP/CE composites. The predicted values suggest that the thermal

conductivity decreases with increased functionalization on GNP due to the GNP defect. However, the thermal conductivities of fGNP/CE models are higher than the thermal conductivities of 2, 3, and 4-layer GNP/CE models which the experiment found that the functionalization improves the dispersion.

The coefficients of linear thermal expansion (CLTE) of GNP/EPON862 system are studied with the similar work flow which the results show the improvement of CLTE regarding to GNP dispersion. Finally, the GNP aspect ratio is included to improve the micromechanical modeling for thermal conductivity.

CHAPTER 1 INTRODUCTION

Carbon fiber/Epoxy composite is an advance material used as the structural component such as aerospace, automotive, high-voltage cable, and sport equipment. This material is very strong, light-weight, chemically resistant, low thermal expansion along the fiber direction. Carbon fiber composite can replace the conventional materials to reduce the weight of product and to improve the chemical resistant. For the vehicle segment, the lighter vehicle uses less fuel which can save the operating cost. For the high-voltage cable segment, the carbon fiber composite core with cycloaliphatic epoxy (CE) in cable can mitigate the thermal sag of cable. This improvement can reduce the chance of accident compared to the conventional cable which elongates and sags at the higher temperature. The carbon fiber composite has been successfully implemented to fabricate the product in the manufacturing scale.

Nevertheless, the carbon fiber composite hardly handles the load transfer in transverse (perpendicular to fiber) direction. The cracks are usually initiated at the interface between epoxy matrix and fiber or in the matrix by itself. There are several researchers who study and improve the mechanical properties in transverse direction. Moreover, the material degradation potentially occurs during the operation due to low thermal conductivity of epoxy matrix. This is because the heat is scarcely dissipated away from the hotspots or the heat source.

To improve the properties of the epoxy matrix as the binder between carbon fibers, the micro particles or nanoparticles are considered to add into the matrix. There are several kind of particles: silicon, metals, carbon black, carbon nanotube, graphene nanoplatelet (GNP), talc, and rubber. Each particle has specifically ability to enhance either thermal or mechanical properties. The mass fraction of these nanoparticles in the composite was studied and some of them showed that the agglomeration of the particle happened at the

high mass fraction of particle. In this research, the study focuses on the CE which is a unique system with GNP due to its superior materials properties.

The objective of this research is to study and predict thermal and mechanical properties of neat cured CE system using molecular dynamics (MD) modeling. The results of neat CE models are validated with experimental values. After the validation, the thermal conductivities of GNP/CE nanocomposites with different levels of GNP dispersions are studied at molecular level using MD modeling. The bulk thermal conductivities of GNP/CE composites and carbon fiber/GNP/CE hybrid composites are further calculated by using micromechanics. The effect of GNP aspect ratio is also investigated in these calculations. The thermal conductivity of covalently functionalized GNP/CE is predicted how the functionalization affects to this property. Moreover, GNP aspect ratio is additionally investigated in micromechanics. Finally, the thermal expansion coefficients of GNP/EPON862 system are also studied by multiscale modeling.

CHAPTER 2 BACKGROUND

The high voltage conductor has been developed for many years because it is very important for transferring electricity to cities, to communities, and to homes. The conventional conductor or the Aluminum Conductor Steel Reinforced (ACSR) has been used for many decades. However, ACSR is not as durable at high temperature which is very dangerous and unreliable due to the thermal expansion of metals. Because the electric transmission needs to be more reliable and more efficient, the Aluminum Conductor Composite Core (ACCC) was developed to replace the ACSR. Both ACSR and ACCC are shown in Figure 1. The outer part of ACSR and ACCC are the aluminum. The core of ACSR is made from steel and the core of ACCC consists of the fiber glass composite and carbon fiber composite which are the yellow and the black color, respectively. Cycloaliphatic epoxy (CE) was used as the binder in carbon fiber composites.

Figure 1 The cross sections of ACSR (left) and ACCC (right), (See Appendix B for copyright agreement).

The thermal expansion of carbon fiber is negative, so the core will not significantly elongate at high temperatures. In Figure 2, the plot shows the cable sags of different conductor's types as the function of temperatures. At 180°C, the ACCC sags less than 5

inches, but ACSR sags more than 60 inches. Apparently, ACCC performs much better in this test. Figure 3 shows the comparison of the structural performance between ACSR and ACCC cables which ACCC cables obviously less sag than the ACSR cables.

Figure 2 Test data of cable sag as a function of temperature, (See Appendix B for copyright agreement).

Figure 3 The comparison of the sag between ACSR and ACCC, (See Appendix B for copyright agreement).

2.1 Molecular Dynamics

Molecular dynamics (MD) is a powerful computational tool to simulate the movement of atoms and molecules and to determine thermal and mechanical properties of materials. The movement in the MD simulation is basically based on Newton's law of motion. The simulation determines the position ($\mathbf{r}$) and velocity ($\mathbf{v}$) vectors of atom i with the time integration using the velocity Verlet algorithm

$$\mathbf{r}_i(t + \Delta t) = \mathbf{r}_i(t) + \mathbf{v}_i(t)\Delta t + \frac{1}{2}\mathbf{a}_i(t)\Delta t^2 \quad (1)$$

$$\mathbf{v}_i(t + \Delta t) = \mathbf{v}_i(t) + \frac{\mathbf{a}_i(t) + \mathbf{a}_i(t + \Delta t)}{2}\Delta t \quad (2)$$

where $\mathbf{a}_i$ is the acceleration of atom i , t is the current time, and Δt is the time step. The acceleration is calculated by

$$\mathbf{a}_i = \frac{\mathbf{F}_i}{m_i} \quad (3)$$

where m_i is mass of atom i , and $\mathbf{F}_i$ is the force vector of atom i obtain from the gradient of the total potential energy (E_{Pot}) on atom i .

$$\mathbf{F}_i = \nabla(E_{Pot})_i \quad (4)$$

The potential energy is depended on the force field that is applied to the system. More details about that force field is given in the next section.

2.1.1 OPLS – All Atom Force Field Parameters

Optimized Potentials for Liquid Simulations (OPLS) – All atom force field [1] was developed by W. L. Jorgensen. This force field is the fix-bonded force field meaning that there is no bond formation and bond scission during the simulation. The potential energies of system are determined from both bonded and non-bonded energies. The bonded

energetic terms include bond stretching, angle bending, and torsional which the graphic representations of bonded energy term are shown in Figure 4. The bond stretching energy is defined by

$$E_{bond} = \sum_{bonds} K_r (r - r_{eq})^2 \quad (5)$$

where K_r and r_{eq} are the stiffness of bond stretching and equilibrium distance constants, r is the current distance between two atoms. The angle bending energy is calculated by

$$E_{angle} = \sum_{angles} K_\theta (\theta - \theta_{eq})^2 \quad (6)$$

where K_θ and θ_{eq} are the stiffness of angle bending and equilibrium angle constants, θ is the current angle on three atoms. The torsional or dihedral energy [2] is computed by

$$E_{torsion} = \sum_{dihedrals} \left[\frac{V_1}{2} [1 + \cos(\phi)] + \frac{V_2}{2} [1 - \cos(2\phi)] + \frac{V_3}{2} [1 + \cos(3\phi)] + \frac{V_4}{2} [1 - \cos(4\phi)] \right] \quad (7)$$

where V_1 , V_2 , V_3 , and V_4 are the Fourier coefficients and ϕ is the dihedral angle.

Figure 4 The graphic representations of (a) bond stretching, (b) angle bending, and (c) torsional.

Van der Waals (VdW) interaction as the non-bonded energy is based on the 12-6 Lennard – Jones [3] interaction

$$E_{ij} = 4\varepsilon \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] \quad (8)$$

where ε is the depth of potential well, σ_{ij} is the equilibrium distances between atom i and atom j , and r_{ij} the current distances between atom i and atom j shown in Figure 5.

Figure 5 The graphic representation of VdW interaction as the non-bonded contribution.

The total potential energy combines all energetic contributions shown as following equation.

$$E_{Pot} = E_{bond} + E_{angle} + E_{torsion} + E_{VdW} \quad (9)$$

2.2 Graphene/Epoxy Composites

Graphene[4] was successfully exfoliated by repeatedly peeling using “Scotch tape” and first characterized in 2004. Graphene is a single layer of graphite with sp^2 carbon atoms. Graphene has the highest thermal conductivity at room temperature which experimentally reported about 5,300 W/mK [5, 6]. This nanomaterial is also the strongest material ever tested which the elastic modulus and tensile strength are equal to 1 TPa and 130 GPa [7], respectively. Because of these promising properties, graphene has been filled into polymer matrix of composites to improve their thermal and mechanical properties.

Many researchers [8-35] experimentally worked on graphene nanoplatelet (GNP)/Polymer composites focused on the mechanical and thermal properties. Thermal conductivities of GNP/epoxy composites were reported in wide range depended on amount of GNP, GNP

aspect ratio, GNP defect density, and GNP dispersion in epoxy. One of the application that requires improved thermal conductivity is thermal interface materials (TIM) as shown in Figure 6. The interface between the TIM and the die or heat sink has the high temperature different meaning the heat cannot be transferred well in this region.

Figure 6 The visual schematic of thermal interface material showing the difficulty of heat dissipation from heat source. Reprinted with permission from [22]. Copyright 2012 American Chemical Society. (See Appendix B for copyright agreement).

The MD modeling was utilized to investigate the characterization and mechanical properties of GNP/EPON862/DETDA system [36, 37] with OPLS – united atom force field. Non-Equilibrium MD (NEMD) was performed to determine the thermal conductivity of GNP/EPON862/TETA system [38-40]. The NEMD method requires a long simulation box which is able to find only thermal conductivity on the long direction. For the GNP/epoxy models, two different models are needed to determine the in-plane and out-of-plane thermal conductivities. To keep the same GNP volume fraction in both models is very challenging. In this research, Equilibrium MD (EMD) approach was selected to determine the thermal conductivity of the nanocomposites. The details of the EMD method is given in Chapter 4.

CHAPTER 3 MD MODELING: PURE CYCLOALIPHATIC EPOXY

3.1 Introduction

Cycloaliphatic epoxies (CE) are commonly used for structural applications requiring improved resistance to elevated temperatures, UV radiation, and moisture relative to Bisphenol A (DGEBA) and Bisphenol F (DGEBF) Diglycidyl Ether epoxies [26, 41, 42]. Thus, CE composites are particularly important in applications such as high-voltage electrical insulators and Aluminum Conductor Composite Core (ACCC) high-voltage power transmission cables, particularly when they are paired with an anhydride curing agent (ACA) which also demonstrates remarkable environmental resistance. ACCC lines must withstand these harsh environmental conditions in addition to localized heating due to transmission line faults (e.g. failing connections and leakage currents). It is imperative that these lines be designed to mitigate localized heating quickly to reduce local material damage. Thus, the composite core component of the ACCC lines should have an optimal level of thermal conductivity. Also, the thermal expansion coefficient should be optimized to mitigate thermal sag in the lines. Accurate and efficient computational models can greatly facilitate the development of these composite core materials to meet these thermal property requirements.

Over the last decade, molecular dynamics (MD) simulation has become an important tool for the prediction of thermo-mechanical properties of epoxy materials. The thermal and mechanical response of DGEBF [37, 43-52] and DGEBA [51, 53-58] crosslinked epoxy systems has been investigated with numerous MD studies. These epoxy systems have become benchmark materials for MD simulation partially due to their relatively simple crosslinking reaction. For CE/ACA, the chain reaction mechanism is much more complex. The only known molecular modeling study for CE/ACA is from Komarov et al. [59], who investigated the system using coarse-grained Monte Carlo simulation for crosslinking,

followed by reversed-mapping to a fully atomistic MD model. Thus, a fully atomistic procedure for modeling the crosslinking of CE/ACA resins has not been developed.

The objectives of this study were to (1) develop an all-atom MD-based modeling procedure to accurately and efficiently simulate the crosslinking process of CE/ACA resins and to (2) predict the bulk-level thermal and mechanical properties of carbon fiber-reinforced CE/ACA composites for a range of carbon fiber volume fractions using a multiscale modeling approach, which includes the MD modeling for atomic length scales and micromechanics for bulk length scales. The modeling procedure was validated with experimental data determined as described herein and from the literature.

This chapter is structured as follows. First, the details of the polymer material system are provided, including the molecular structures of the resin and hardener and the curing mechanism. Second, details are provided about the multiscale modeling procedure. Third, the experimental methods for measurement of the mass density, elastic properties, glass-transition temperature, and thermal conductivity are described. Finally, the modeling results are discussed with respect to the experimental values.

3.2 Materials systems

Epoxy cyclohexyl methyl 3,4 epoxy cyclohexyl carboxylate (EEC) is a CE resin as characterized by the aliphatic carbon rings fused to reactive epoxide groups. For EEC, there are two epoxide groups per molecule as shown in Figure 7. The ACA is 4, 7-Methanoisobenzofuran-1, 3-dione, 3a, 7, 7a-tetrahydromethyl which contains a cyclic anhydride ring and bi-cyclic component, also shown in Figure 7.

Figure 7 Molecular structure of EEC (left) and ACA (right).

The curing mechanism [60, 61] of the EEC/ACA system consists of two main alternating reactions: an esterification reaction and a cyclic anhydride ring opening reaction. Figure 8 shows the esterification reaction between an epoxide group and carboxyl group, which requires a catalyst to start the reaction. This reaction generates an ester chain and hydroxyl group that is necessary for opening the cyclic anhydride ring. Figure 9 shows the cyclic anhydride ring opening reaction. This reaction is initiated by a hydroxyl group from the esterification reaction. A carboxyl group is created and continues again as the reactive group in the esterification reaction. Both reactions continue until all nearby reactive groups are reacted.

Figure 8 Esterification reaction between carboxyl and epoxide groups.

Figure 9 Cyclic anhydride ring opening reaction between hydroxyl group and anhydride ring.

3.3 Computational Details

The multi-scale computational approach employed in this study includes both MD and Micromechanical modeling. MD modeling was used to determine thermal properties of the neat epoxy based on the molecular structure. For the micromechanics modeling, the results from the MD modeling were used as input into a larger-scale Representative Volume Element (RVE) to predict the effective thermal conductivity of carbon fiber/CE composites. All details of the modeling are given in this section.

3.3.1 Monomers

All neat epoxy models were simulated at the molecular level using the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) MD software package [62] with the OPLS - AA (Optimized Potentials for Liquid Simulations - All Atom) force field [1, 63]. Monomeric structures of EEC and ACA were initially created using ChemBioDraw [64] and subsequently imported into LAMMPS. The force constants associated with bond, angle, dihedral, and van der Waal (vdW) interactions were used. The topology of both monomers were equilibrated using the Conjugated-Gradient method, as implemented in LAMMPS, with a 1×10^{-4} energy tolerance. MD simulations were subsequently performed with the NVT ensemble for 1 ns with 1 fs time steps. In Figure 10, the resulting molecular structures of EEC and ACA monomers were rendered using the Open Visualization Tool (OVITO) software package [65].

Figure 10 Molecular models of EEC (left) and ACA (right). Red: oxygen, black: carbon, white: hydrogen.

For the simulated crosslinking, the curing mechanism discussed above required a catalyst to start the chain reaction. A sub-set of the ACA molecules were modified with an ethanol molecule [66], as shown in Figure 11. The cyclic anhydride ring on the ACA molecule was opened with the hydroxyl group on the ethanol molecule. The exposed carboxyl group was therefore available to react with epoxide groups for the esterification reaction (Figure 2).

Figure 11 Molecular structure and molecular model of modified ACA. Red: oxygen, black: carbon, white: hydrogen.

Bulk molecular models of the EEC/ACA system were generated using a multi-step process. The molar ratio between the CE resin and ACA was 1:2. The monomers of EEC, ACA, and modified ACA were mixed as shown in Table 1. These monomers were combined in a large MD simulation box. The initial mass density of the simulation box was less than 0.008 g/cm^3 and all boundaries were periodic. For the results discussed herein, all thermal properties were determined from a cubic simulation box, except for the thermal conductivity simulations with direct method (described below), which utilized a prism-shaped simulation box.

Table 1 The number of molecules and atoms of cubic and prism simulation boxes.

Shape	Number of molecules			Number of atoms
	EEC	ACA	Modified ACA	
Cube	84	156	12	7,164
Prism	126	234	18	10,746

The simulation boxes were alternately subjected to potential energy equilibrations and simulation box size reductions using the “minimize” and “fix deform” commands in LAMMPS, respectively. The simulation boxes were gradually compressed to a density of 1.2 g/cm³, which is the accepted bulk density of most epoxy resins [67]. The box lengths in along the x, y, and z directions were sequentially reduced to their final length by densifying in four different steps as shown in Table 2 over a total simulation time of 4.2 ns with 1 fs time steps. The density profiles of the densified models were spatially uniform along the x, y, and z directions, and thus the MD models were well-equilibrated in the uncrosslinked state.

Table 2 The length of the cubic and prism-shape simulation boxes during the densification.

Step	Cube (Å)			Prism (Å)			Time (ns)
	x	y	z	x	y	z	
0	300.00	200.00	200.00	300.00	300.00	300.00	-
1	41.50	41.50	41.50	26.15	26.15	156.88	0.2
2	23.86	23.86	23.86	15.03	15.03	90.20	1.0
3	21.79	21.79	21.79	13.73	13.73	82.36	2.0
4	20.75	20.75	20.75	13.07	13.07	78.44	1.0

3.3.1.1 Crosslinking Process

The crosslink process was iterative process combining LAMMPS and Python script. For this approach, the crosslink density can be specified which 60%, 65%, 70%, 75%, 80%, 85%, and 90% crosslink percentage of EEC/ACA system were aimed in this work.

Schematic 1 shows the simulated crosslinking process with MD steps labeled as “LAMMPS” and the “Python” labels corresponding to Python scripting designed to delete and create all bonds, angles, and dihedrals. The Python scripts also updated pair coefficient of relative atoms. The labels “1” and “2” correspond to the esterification reaction (Figure 2) and cyclic anhydride ring opening (Figure 3) reactions, respectively. Following the densification, the data file for the densified model was used for LAMMPS 1 to initially

create the carbon-oxygen bond in the esterification reaction. The updated data file was subsequently used for the Python 1 step to create and delete all related bonds, angles, and dihedrals. Following this, the data file was run in the LAMMPS 2 step to initially generate the oxygen-hydrogen bond of the cyclic anhydride ring opening reaction and Python 2 updated all information for this reaction in the same manner as Python 1.

Schematic 1 Crosslinking process of EEC/ACA

The crosslink percentage was calculated in the Python 2 step by dividing total number of formed ester bonds by the total number of epoxide groups at the beginning of the crosslinking process. The data files which were close to 60%, 65%, 70%, 75%, 80%, 85%, and 90% of crosslink percentage were exported to different folders to study the effect of crosslink density on materials properties. After the Python 2 step was completed, the current crosslinking step was complete and the structure file was passed back to LAMMPS 1 for subsequent crosslinking steps. After one hundred cycles, the structure file was equilibrated in the NPT (constant pressure and temperature) ensemble for 1 ns with 1fs time steps. If the crosslink density was less than 90%, the structure file was imported back into the LAMMPS/Python steps for another 100 cycles. Once the crosslink percentage was equal to or greater than 90%, the crosslinking process was completed and the model was fully equilibrated with the NPT ensemble as mentioned above. The details of LAMMPS 1, Python 1, LAMMPS 2, and Python 2 steps are provided below.

The LAMMPS 1 step initially created the bond between carbon atom and oxygen atom from epoxide and carboxyl groups, respectively, by using ‘fix bond/create’ command and creating the bond every time step with 0.001 probability within a 7 Å threshold. The NVT ensemble was applied at 300 K, which ran for 200 fs with 0.1 fs time steps. The Python 1 step created the bond between the oxygen and hydrogen atoms from epoxide and carboxyl groups, respectively, which provided the hydroxyl group. The old bonds, which were carbon-oxygen in the epoxide group and oxygen-hydrogen in the carboxyl group, were assigned to be a special bond type for deletion in the LAMMPS 2 step, along with the associated angles and dihedrals.

The LAMMPS 2 step began with generating the bond between the oxygen and hydrogen atoms from cyclic anhydride ring and hydroxyl group, respectively, in the same manner as LAMMPS 1. The Python 2 step established the shorter-distanced bond between the carbon and oxygen atoms from anhydride ring and hydroxyl group, respectively. The shorter-distanced bond can prevent any over-stretch bond. The oxygen-hydrogen and carbon-oxygen bonds from the hydroxyl group and anhydride ring, respectively, were assigned for

deletion in the LAMMPS 1 step. All angles and dihedrals were updated in the same manner as with Python 1. For LAMMPS 1 and LAMMPS 2, the special bond is removed at the beginning of script by using “delete_bond”.

3.3.1.2 Equilibration

After the crosslinking process, the models were equilibrated with the NPT ensemble at 1 ATM and 300 K to allow residual stresses to be minimized. Figure 12 shows representative mass density profiles along each of the Cartesian axes. The relatively small fluctuations in density indicate that the model has minimal localized residual stresses within the simulation box. The mass density was calculated from averaging the last 10 ps of each simulation. The average mass densities and conversion levels are provided in Table 3. Figure 13 shows a representative crosslinked model after equilibrating for 2 ns with 1 fs time steps. After crosslinking, the models were ready for further simulation to predict the thermal properties.

Table 3 The crosslink densities and mass densities of models and experiments.

Cube		Prism	
Crosslink density	Mass Density (g/cm ³)	Crosslink density	Mass Density (g/cm ³)
0.60 ± 0.00	1.211 ± 0.003	0.60 ± 0.00	1.209 ± 0.005
0.66 ± 0.01	1.214 ± 0.006	0.65 ± 0.00	1.206 ± 0.004
0.70 ± 0.00	1.210 ± 0.004	0.70 ± 0.00	1.207 ± 0.005
0.75 ± 0.01	1.204 ± 0.004	0.75 ± 0.00	1.204 ± 0.005
0.80 ± 0.00	1.199 ± 0.006	0.80 ± 0.00	1.193 ± 0.005
0.85 ± 0.00	1.191 ± 0.006	0.85 ± 0.00	1.187 ± 0.005
0.90 ± 0.00	1.183 ± 0.007	0.90 ± 0.01	1.187 ± 0.001

Figure 12 Density profiles of 80% crosslink cubic EEC/ACA model after equilibration along x, y, and z direction.

Figure 13 A representative crosslinked cubic model of EEC/ACA after equilibration.

3.3.2 Deformation Models

Elastic properties were determined by uniaxial tensile deforming the crosslinked models.

$$E_x = \frac{\sigma_x}{\varepsilon_{xx}} \quad (10)$$

As shown above, the isotropic Young's modulus was calculated from the initial slope of true stress/true strain plot in x, y, and z directions and averaged all directions. The MD models were deformed uniaxially using the “fix deform” command in LAMMPS with an engineering strain rate of $1 \times 10^8 \text{ s}^{-1}$. For a given deformation along a principal direction, the lateral dimensions of the simulation box were allowed to have the natural Poisson's contraction by setting 1 ATM pressure with the NPT ensemble at 300 K. These simulations ran for 2 ns with 1 fs time steps. During the simulations, all stresses and strains of the models were averaged every 4 ps. Figure 14 shows a representative plot for determining the slope using linear regression on the data that was below a strain of 0.04. The Poisson's ratio was calculated from negative slope of transverse and axial strain plot shown in Figure 15.

Figure 14 A representative simulated stress/strain plot of EEC/ACA.

Figure 15 A representative Poisson's ratio from the slope between transverse and axial strain

$$G_{xy} = \frac{\tau_{xy}}{\gamma_{xy}} \quad (11)$$

The simulation boxes were also subjected to shearing deformations, and the shear modulus was determined from the initial slope of the shear stress (τ) and engineering shear strain (γ) response using Equation (5). The boxes were deformed using the ‘fix deform’ command in LAMMPS in the xy, xz, and yz planes in individual simulations. Each simulation ran for 2 ns with 1fs time steps.

3.3.3 Thermomechanical Models

3.3.3.1 Glass-Transition Temperature

The glass transition temperature was determined for each crosslink density using the method of Bandyopadhyay et al. [46]. The temperature of the crosslinked cubic EEC/ACA simulation boxes was increased from -100 to 527 °C (173 – 800 K) in the NPT ensemble

under 1 atm pressure. The model was gradually heated over 5 ns with 1 fs time steps. The heating rate was 1.25×10^{11} °C/s. The mass densities and temperatures of the MD models were averaged every 2 ps throughout the simulations and plotted as shown in Figure 16 for a representative system. The two linear trend lines were fit using the “segmented” package [68] in the RStudio [69] integrated development environment. The glass-transition temperature was defined as the temperature corresponding to the interception of the trend lines.

Figure 16 Plot of mass density vs temperature for determining glass-transition temperature for a EEC/ACA model of 80% crosslink density.

3.3.3.2 Coefficient of Linear Thermal Expansion

The coefficient of linear thermal expansion (CLTE) was determined using the same output from the heating-up simulations for the glass-transition temperature. Specifically, the CLTE was calculated from

$$\alpha = \frac{\beta}{3} = \frac{1}{3} \left(\frac{1}{V} \frac{\partial V}{\partial T} \right) \quad (12)$$

where β is the coefficient of volumetric thermal expansion (CVTE). For each simulation, the system temperatures and volumes were averaged every 2 ps. Figure 17 shows a representative plot between volume and temperature. A polynomial function of volume, $V(T)$, was fit to the data and differentiated with respect to the temperature (T) for Equation (12). In this study, the CLTE was calculated at 300K (27 °C) for each of the crosslinking levels.

Figure 17 Plot of simulation box volume as a polynomial function of temperature from a representative 80% crosslinked cubic model with the polynomial trend line (solid line) and tangent line (dashed line) at 27°C.

3.3.4 Thermal Conductivity Models

The thermal conductivities of the crosslinked models were determined by two different methods. The first method was the Non-Equilibrium MD (NEMD) approach, also known as the direct method based on Fourier's law. The second method was the Equilibrium MD (EMD) approach based on the fluctuation-dissipation theorem, also known as the Green-Kubo [70] formalism. Both methods have been previously used to predict the thermal conductivities of Si [71] and EPON862 epoxy [45].

3.3.4.1 Non-equilibrium Molecular Dynamics

The NEMD method requires a steady-state condition, and the thermal conductivity is calculated using

$$\kappa = -\frac{J}{dT/dz} \quad (13)$$

where J is the heat flux (rate of heat flow per unit area) and dT/dz is the temperature gradient along the z-direction. A prism-shaped MD simulation box was used to predict the thermal gradient. Figure 18 shows a representative system with an aspect ratio of 6 which this configuration was developed by Varshney et al. [72]. The prism model was divided into 20 equally-sized slabs along the length. The positions of the atoms in the slabs on both ends of the simulation box were fixed. The temperatures of the slabs next to the end slabs were held at 250 and 350 K (red and blue slabs in Figure 19, respectively) using the NVT ensemble with 5 fs of temperature damping to obtain an overall temperature of 300K. The energies of the middle slabs were conserved with the NVE ensemble. The heat flux was calculated using

$$J = \frac{(Q_{hot} - Q_{cold})/2}{At} \quad (14)$$

The total heat ($Q_{hot} - Q_{cold}$) was divided by 2 because the heat was transferred to both sides of the simulation box. The NEMD simulation ran for 4 ns with 1 fs time steps. The first 2 ns of the simulation established the temperature gradient into a steady state condition. The final 2 ns of the simulation was used to determine the average temperature in each slab as well as the inlet and outlet energies for calculating the thermal conductivity using Equation (13).

Figure 18 A representative prism-shaped model for determining the thermal conductivity using NEMD.

Figure 19 Simulation box including fixed slabs (grey), 350 K slab (red), 250 K slab (blue), and middle slabs (white).

3.3.4.2 Equilibrium Molecular Dynamics

The EMD method is based on Green-Kubo formalism which is capable to calculate several transport coefficients such as viscosity, self-diffusion coefficient, thermal conductivity, etc. For the thermal conductivity, Green-Kubo [70] expression is shown in following equation.

$$\kappa_x = \frac{V}{k_B T^2} \int_0^\infty \langle J_x(0) J_x(t) \rangle dt \quad (15)$$

where V is the system volume, k_B is the Boltzmann constant, T is the system temperature, and $\langle J_x(0) J_x(t) \rangle$ is the heat current autocorrelation function (HCACF). The EMD method can determine the thermal conductivity of an isotropic material by averaging the properties along the x, y, and z axes using

$$\kappa = \frac{V}{3k_B T^2} \int_0^{t_c} \langle \mathbf{J}(0) \cdot \mathbf{J}(t) \rangle dt \quad (16)$$

where the heat flux vector is

$$\mathbf{J} = \frac{1}{V} \left[\sum_i E_i \mathbf{v}_i - \sum_i \mathbf{S}_i \mathbf{v}_i \right] \quad (17)$$

where

$$E_i = \frac{1}{2} m_i v_i^2 + \frac{1}{2} U_i \quad (18)$$

where the first term is the total kinetic energy; $\mathbf{v}_i$ and m_i are the velocity vector and mass of atom i , respectively; and U_i is the total potential energy of atom i which includes the 12 - 6 Lennard-Jones potential for van der Waals interactions. The bonded interactions include the stretching (bond), bending (angle), and torsional (dihedral) energies. $\mathbf{S}_i$ in Equation (17) is the per-atom stress tensor of atom i .

Cubic MD simulation boxes were used to determine thermal conductivities via the EMD method by initially maintaining the temperature at 300 K with the NVT ensemble. The simulations ran for 10 ps with 1 fs time steps with a 10 Å Lennard-Jones cutoff. The “compute heat/flux” command in LAMMPS was utilized to compute the heat flux from the potential energy, kinetic energy, and stress values. The HCACF was obtained by using the autocorrelation average with the ‘fix ave/correlate’ command in LAMMPS.

Figure 20 Representative plot of the normalized HCACF and thermal conductivity of the CE system as a function of autocorrelation time (t_c).

The integral term in Equation (16) was calculated using the trapezoidal rule for 50 ps of the correlation time (t_c) with 5 fs time increments. The fluctuation of the HCACF decayed to zero after 4 ps, as shown in Figure 20. The data in the figure suggests that the correlation time ($t_c = 50$ ps) is sufficiently large for this system. The total simulation time used to determine the thermal conductivity was 10 ns in order to have sufficient statistical averaging. The thermal conductivity of the EEC/ACA system was calculated from equation

(16) and is shown in Figure 20. The thermal conductivity was averaged from the final 10 ps of the correlation time.

3.3.5 Micromechanics

The effective elastic modulus and bulk thermal conductivity of the unidirectional carbon fiber/CE composite was predicted using micromechanics calculations. Specifically, the thermal conductivities of the epoxy matrix were taken from the MD simulations described above and the AS4 carbon fiber properties were taken from the literature [73, 74] shown in Table 4. The uncertainties in the elastic properties and thermal conductivities for the neat epoxy represent the standard deviation from the multiple MD predictions. Three different values of the properties of the neat epoxy were used in the micromechanics predictions: the mean value and the mean value $\pm$ one standard deviation. This provided the uncertainty in the properties at the bulk level based on the uncertainty at the molecular level.

The Micromechanics Analysis Code based on the Generalized Method of Cells (MAC/GMC) [75] was used for the micromechanics predictions. A circular fiber approximation (rectangular pack or ‘Architecture 13’ as implemented in MAC/GMC) was used as a repeating unit cell (RUC). This RUC has 26×26 subcells in which 312 middle subcells represented the fiber region and the other subcells represented the matrix region. The calculation of the effective elastic modulus and thermal conductivities of the Carbon fiber/CE composite included fiber volume fractions ranging from 5% to 80% with 5% increments.

Table 4 Materials properties of neat CE and carbon fiber.

Properties	Neat CE (EEC/ACA)	Carbon Fiber (AS4)
E_A (GPa)	2.38 ± 0.35	235
E_T (GPa)	2.38 ± 0.35	15
ν_A	0.38 ± 0.03	0.2
ν_T	0.38 ± 0.03	0.07
G_A (GPa)	0.82 ± 0.15	27
k_A (W/mK)	0.24 ± 0.02	6.50
k_T (W/mK)	0.24 ± 0.02	2.18

3.4 Experimental Testing

3.4.1 Fabrication of neat CE*

The EEC/ACA neat epoxy [76] was fabricated using a FlackTek SpeedMixer DAC 150.1 FVZ by pouring resin and hardener in a 100 g : 138 g ratio into 5 mixing cups of 90 g each, for a total batch size of 450 g. Each cup was mixed in the SpeedMixer for 2 minutes at 2500 rpm. The cups were degassed at 100 °C and 29 inHg vacuum until no more bubbles appeared. The mixture was then poured into a pre-heated mold and degassed again under full vacuum. The mold was coated with Mann Ease Release 300. For the neat epoxy, the preheating and final degassing were performed at 100 °C. The curing cycle for all the epoxy specimens was 100 °C for 1 hour, then heated to 200 °C at 2°C/min, then held at 200 °C for two hours. The oven was turned off and the cured epoxy was allowed to cool in the oven to room temperature at a ~1 °C/min cooling rate. The molds made about 20 rectangular bars (165 mm long by 19 mm wide by 3.3 mm thick) and 5 disks (64 mm diameter and 3.2 mm thick), from which the testing specimens were machined. The density of the samples was measured at 23 °C according to ASTM D792 [77].

3.4.2 Tensile Testing*

The tensile properties (at 23 °C, ASTM type I sample geometry) were measured according to ASTM D638 [78] at a crosshead rate of 1 mm/min. An InstruMet Sintech screw-driven mechanical testing machine was used with an axial extensometer to collect strain values. The tensile strength, strain, and modulus [76] were measured at 23 °C.

3.4.3 DMA testing for glass-transition temperature*

Dynamic Mechanical Analysis (DMA) was used to find the glass-transition temperature of the epoxy samples. The tests were conducted with a TA Instruments Q800 DMA using the dual/single cantilever clamp. The single cantilever geometry was used for all testing, with

* This section was performed and wrote by Julie M Tomasi.

a set length of 17.5 mm between clamps. The sample dimensions were 3.3 mm thick, 12 mm wide, and 35 mm long; and were cut from the rectangular bars. Samples were rinsed with isopropyl alcohol before testing. Each sample was loaded into the clamps and tightened down using 8 in-lb of torque. Tweezers were used to keep the sample surfaces free of oil from hands and fingers.

Once the samples were in placed in the clamps, amplitude sweep tests were performed. The test mode was set to “DMA Multi Strain” with the test set to “Strain Sweep”. The frequency was kept at 1 Hz with the isothermal temperature at 35 °C and a soak time of 5 minutes. The amplitude was swept from 5 μm to 50 μm . Following these tests, graphs of amplitude versus loss modulus were analyzed to determine the amplitude needed for the temperature sweep test.

To determine the storage modulus, loss modulus, and tan delta, the program mode was set to “DMA multi frequency strain” and the test protocol was set to “temp ramp/frequency sweep”. The procedure parameters included an amplitude of 30 μm , an initial temperature of 50 °C with a soak time of 5 minutes, a temperature ramp rate of 3 °C/min, and a final temperature of 290 °C with a hold time of 5 minutes. The frequency was held at 1 Hz for the entire duration of the tests. Once the tests were completed, the data was analyzed to determine the storage modulus, loss modulus, and tan delta values for the entire temperature range. The temperature at the peak of the tan delta graph provided the glass transition temperature.

3.4.4 Thermal Conductivity Testing*

Through-plane thermal conductivity was measured using a Holometrix Model TCA-300 Thermal Conductivity Analyzer, which follows the ASTM F433 [79] guarded heat flow meter method. The though-plane thermal conductivities of the 3.2 mm thick, 50 mm diameter disc-shaped test specimens were measured at 55 °C.

* This section was performed and wrote by Julie M Tomasi.

3.5 Results

3.5.1 Mass Density

The average mass densities of the cubic and prism models of cured EEC/ACA system at each crosslink density are shown in Table 3. The mass density values are in good agreement with the experimentally obtained value of $1.219 \pm 0.001 \text{ g/cm}^3$. In general, the predicted mass densities of both cubic and prism MD models decreased with increases in crosslink density. The mass density reduction is likely a result of the decrease in chain flexibility with increased in crosslink density. At lower crosslink densities, the monomers can be positioned closer together with little constraint. At higher crosslink densities, the additional covalent bonds between monomers increase constraining forces, thus prohibiting full structural densification.

3.5.2 Mechanical Properties

For mechanical properties of EEC/ACA system, five crosslinked models are different EEC/ACA models from the models for thermal properties. These models were crosslinked by only 100 cycles of crosslink shown in Schematic 1. The average crosslink density and mass density of EEC/ACA system for mechanical properties are shown in Table 5. The mass density is good agreement with the experimental value ($1.219 \pm 0.001 \text{ g/cm}^3$).

Table 5 The average elastic properties of EEC/ACA from MD.

Properties	Value
Crosslink density	0.74 ± 0.06
Mass density (g/cm^3)	1.208 ± 0.010
E (MPa)	2328 ± 351
G (MPa)	816 ± 152
ν	0.38 ± 0.03

The predicted elastic properties are shown in Table 5, which are averaged over five replicate models in all three Cartesian directions. Figure 21 shows the Young's modulus as a function of crosslink density, as well as the experimental value which the crosslink density is unknown. The Young's modulus of the 0.79 and 0.80 of crosslink-density models, which is about 2700 MPa, agrees well with the Young's modulus from experiment.

Figure 21 Plot of Young's modulus as a function of crosslink density compared with experiment [76].

Figure 22 shows the predicted axial and transverse elastic modulus of carbon fiber/EEC/ACA composites. The standard deviations of axial elastic modulus are relatively small which the error bars are hidden in the data points. For the transverse direction, the standard deviations are shown in the plot. These predicted axial and transverse elastic modulus are in good agreement with the experimental values form Kilmek-McDonald [80] which validate the multiscale computational method modeling for carbon fiber/CE system.

Figure 22 Predicted axial and transverse elastic modulus as the function of carbon fiber volume fraction. Experimental values of carbon fiber/EPON862 composites are obtained from Kilmek-McDonald [80].

3.5.3 Thermal Properties

3.5.3.1 Glass-Transition Temperature

Figure 23 Predicted glass-transition temperatures of cured epoxy models as a function of crosslink density. Experimentally obtained value (with unknown crosslink density) is overlaid on the data.

Figure 23 shows the glass-transition temperature averaged over five different models for each crosslink density. The plot shows that the glass-transition temperature is crosslink density dependent, as was previously observed with the EPON862 system [46]. The experimental glass-transition temperature (dashed line) was 250.58 ± 1.05 °C. The experimental heating rate is about 12 order of magnitude slower than the heating rate in MD simulation. Due to the heating rate effect, the glass-transition temperature increases 3 °C when the heating rate increases an order of magnitude [47, 81]. The adjusted glass-transition temperature (solid line) is corrected by adding 36 °C to the experimental (original) value. The predicted glass-transition temperature for 85 and 90% crosslink densities are in good agreement with the experiment, for which the crosslink density is not known.

3.5.3.2 Coefficient of Linear Thermal Expansion

Figure 24 shows the predicted CLTE of the epoxy as a function of crosslink density at 300K. A range of experimental CLTE values from the literature [82-86] (with unknown crosslink density) are included in the plot. The plot demonstrates that the predicted CLTE decreases with increasing crosslink density. A similar trend for the CLTE of a CE system was observed by Komarov et al. [59]. From the figure it is also evident that the predicted CLTE values approach the experimental values at increasing levels of crosslink density. Because most epoxies are expected to have relatively high crosslink densities, there is satisfactory agreement between models and literature values.

Figure 24 Plot of predicted CLTE as a function of crosslink density at 300 K. Literature (experiment) values of unknown crosslink density are overlaid and predicted values from literature are also included.

3.5.3.3 Thermal Conductivity

Figure 25 Plot of NEMD and EMD thermal conductivities as a function of crosslink density compared with experiments (Blue region [87-93] and orange line [76]).

Figure 25 provides the predicted average thermal conductivities of the CE epoxy system averaged over the five models using the EMD and NEMD methods. The error bars represent the standard deviations associated with the five models at each crosslink density. Given the uncertainty levels, the results suggest that the two methods are in general agreement. The thermal conductivity from NEMD is dependent on the crosslink density but the EMD cannot capture the crosslinking dependence. This behavior is similar to that observed with MD modeling of the EPON862 system [45]. The results also suggest that the predicted thermal conductivities are within the range of the experimental thermal conductivity values reported in the literature [87-93]. However, the predicted thermal conductivities are significantly higher than those from the experiment [76] described herein. The source of the discrepancy is uncertain, however, it is clear that the agreement with the literature values serves as a validation of the simulation techniques.

Figure 26 Plot of thermal conductivity as a function of carbon fiber volume fraction parallel (circle) and transverse (triangle) to the fiber direction. Experimental values taken from Villière et al. [94-97].

Figure 26 shows the predicted thermal conductivities of a unidirectional EEC/ACA/carbon fiber composite parallel (k_{11}) and transverse ($k_{22}=k_{33}$) to the fiber direction. The effective axial and transverse thermal conductivities increase linearly and nonlinearly, respectively, with the carbon fiber volume fraction. The standard deviations of these calculations are relatively small and the corresponding error bars are partially hidden by the data points in Figure 26. The predicted thermal conductivities are in good agreement with experimental values from the literature [94-97], thus further validating the multiscale computational modeling method.

3.6 Conclusions

There are two important results from this chapter. First, an all-atom MD modeling method for CE epoxies was developed and validated with comparison to experimental data for glass transition temperature, CLTE, and thermal conductivity. To the best of the authors' knowledge, this is the first such method developed specifically for CE epoxies. Second, the multiscale modeling approach developed in this study, which uses results of MD and micromechanical modeling, can accurately predict the bulk-level thermal conductivity of CE-based composite materials. The multiscale approach was validated with comparison of predicted thermal conductivity values of epoxy/carbon fiber composites to those found in the literature.

The developed multiscale modeling method can be used to facilitate the development of CE-based epoxy composites and nanocomposite materials for thermal applications. By taking advantage of low-cost simulations to establish preliminary material designs, overall materials development costs can be dramatically reduced and development times can be expedited. This ability to efficiently develop new CE-based composite materials is particularly important for the continued development of ACCC high-transmission power lines.

CHAPTER 4 MULTISCALE MODELING: THERMAL CONDUCTIVITY OF PRISTINE GRAPHENE NANOPLATELET/CARBON FIBER/CYCLOALIPHATIC EPOXY HYBRID COMPOSITES

4.1 Introduction

Because cycloaliphatic epoxies (CE) have excellent chemical resistance and a high glass-transition temperature relative to other polymers used in composite materials, they are commonly used for applications with aggressive environments. Carbon fiber (CF)/CE composites have been used as structural reinforcement in aluminum conductor composite core (ACCC) [98] high-voltage power lines resulting in a six-fold reduction of high temperature sag when compared with the conventional aluminum conductor steel-reinforced (ACSR) cable. ACCC lines must be able to endure extreme weather conditions and localized heating due to transmission line faults. However, CE has very low thermal conductivity. To improve the material resistance to localized heating (or hotspots), we seek to increase the thermal conductivity of the CE matrix by incorporating conductive nanofillers.

Graphene Nanoplatelet (GNP) reinforcement has been shown to improve the mechanical properties in the transverse direction of GNP/CF/Epoxy hybrid composite layers [33, 36] and increase the thermal conductivity [11, 14, 15, 22, 24, 27-31, 40]. This is because of the superior mechanical and thermal properties of pristine graphene. The Young's modulus of graphene is equal to 1 TPa [7], and the in-plane thermal conductivity is about 1,000 – 5,300 W/mK [5, 6, 99]. GNP has capability to enhance the thermal conductivity of the CE system.

However, it is still unclear the degree to which GNP dispersion affects the composite thermal conductivity of CE-based composites. An accurate model can establish what conductivity values are expected given perfect GNP dispersion. Knowing the ideal case

would enable experimentalists to better assess the dispersion of their samples and determine whether improved dispersion is desirable or if the benefits are likely minimal. Recently, a method was developed by Chinkanjanarot et al. [100] to predict the thermal conductivity of neat CE resins using molecular dynamics (MD) simulation, specifically, a non-equilibrium MD (NEMD) approach. The NEMD can predict the thermal conductivity of neat CE model good agreement with experiment. Although this method works nicely for isotropic polymer resins, it can only determine the thermal conductivity in one particular direction for a single simulation and typically requires an elongated simulation box. Applying NEMD to anisotropic materials necessitates several separate simulations to determine the directional-dependent conductivity, and multiple elongated boxes having the same GNP mass fraction may be needed. Thus, it is difficult to use NEMD in modeling composite materials. Alternatively, Equilibrium Molecular Dynamics (EMD) can be used to determine the three-dimensional thermal conductivity in a single simulation and requires a standard cubic simulation box. The EMD method has been used to successfully study the thermal conductivity of epoxy systems [45, 57].

In this study, the objective is to predict the bulk thermal conductivity of fully cured GNP/CE nanocomposites and GNP/CF/CE hybrid composites using a multiscale modeling approach (including MD, randomization, and micromechanics). The influence of GNP dispersion and GNP concentration on the effective thermal conductivity is analyzed. The predicted thermal conductivities compare well with the literature experimental values. The results show that the dispersion of GNP directly influences the transverse thermal conductivity of the hybrid composites.

4.2 Computational Details

The multiscale modeling scheme is shown in Figure 27. The thermal conductivity of GNP/CE nanocomposites was initially determined at the molecular level by MD. The effective nanocomposite thermal conductivity was obtained by randomization and then

scaled with different amounts of GNP by micromechanics. The effective thermal conductivity of GNP/CF/CE hybrid composites was also determined by using micromechanics.

4.2.1 Molecular Modeling

All Molecular Minimization (MM) and MD simulations were performed on Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) [62] with Optimized Potential for Liquid Simulation All Atom (OPLS-AA) [63] force field. All molecular graphics were rendered by using Open Visualization Tool (OVITO) [65].

Figure 27. Schematic of multiscale modeling. Red: oxygen, black: carbon, white: hydrogen.

The molecular structures of epoxy cyclohexyl methyl 3,4 epoxy cyclohexyl carboxylate (EEC), which is a CE resin, and the anhydride curing agent (ACA) were created by using a similar procedure described in previous studies [26, 46, 50, 100]. The molecular structure

of Modified ACA [100], which is necessary to initiate curing, was also created using the same method. The molecular structures of these monomers are shown in Figure 28.

4.2.1.1 GRAPHENE MD MODEL

Graphene was created by using the *lattice* command in LAMMPS. The lattice vectors were $a_1(1, 0, 0)$, $a_2(0, 1.732, 0)$, $a_3(0, 0, 3.350)$ with 2.46 Å lattice length [101]. The basis of each carbon atom is given in Table 7. Graphene models of 1, 2, 3, and 4 layer(s) of graphene were built with 576 atoms per layer. The molecular structure of double-layer GNP is shown in Figure 28. Bonds, angles, and dihedrals were determined through the periodic boundary. All graphene models were equilibrated with NVT at 300K. A cutoff radius of 10 Å was selected for pairwise interactions. The equilibration was run for 1 ns with 1 fs time steps.

4.2.1.2 NEAT CE AND GNP/CE MODELS

The CE system was combined with graphene as shown in Figure 28. In the CE system, the molecular ratio of the EEC, ACA, and modified ACA molecules was 7 : 13 : 1 representing the stoichiometry between CE and anhydride molecule which is 1 : 2, respectively. Since all models in this research were set to be cubic, the ratio of atoms between GNP and CE depended on the number layers of GNP as listed in Table 7. Prior to forming the cubic model, the CE and GNP were placed into a long box. For the neat CE model, all EEC, ACA, and modified ACA were combined without GNP.

Table 6 The factional coordinates of carbon atom in graphene unit cell.

No. of basis atom	Fractional coordinates
1	(0, 0, 0)
2	(0.5, 1.667, 0)
3	(0.5, 0.5, 0)
4	(0, 0.667, 0)
5	(0, 0.333, 0.5)
6	(0.5, 0.5, 0.5)
7	(0.5, 0.833, 0.5)
8	(0, 0, 0.5)

Table 7 The numbers of total atoms and GNP mass fraction of each system.

System	GNP atoms	CE atoms	Total atoms	GNP mass fraction
Neat CE	0	7,164	7,164	0.000
1GNP/CE	576	5,373	5,949	0.151
2GNP/CE	1,152	4,776	5,928	0.287
3GNP/CE	1,728	4,179	5,907	0.408
4GNP/CE	2,304	3,582	5,886	0.517

The long simulation box was alternately compressed between energy minimization and box compressing by “fix deform” command along with NVT ensemble. The final lengths of pre-crosslinked simulation box for each system are shown in Table 8. The densification performed with four different compressing steps shown in Table 9 which ran for 5.2 ns with 1 fs time steps. The stepwise technique prevented the residual stress of the model during the densification. Five different model of uncrosslinked GNP/CE were obtained for each system.

Table 8 The length of the simulation boxes after the densification.

System	Final length of densified box (Å)		
	x_f	y_f	z_f
1GNP/CE	38.69	37.70	36.18
2GNP/CE	38.69	37.70	36.05
3GNP/CE	38.69	37.70	35.92
4GNP/CE	38.69	37.70	35.79

Table 9 The length ratio of the cubic and prism-shape simulation boxes during the densification.

Step	Length ratio			Time (ns)
	x	y	z	
1	$4x_f$	$4y_f$	$4z_f$	1.2
2	$1.15x_f$	$1.15y_f$	$1.15z_f$	2
3	$1.05x_f$	$1.05y_f$	$1.05z_f$	1
4	x_f	y_f	z_f	1

Figure 28. Combining of EEC, ACA, modified ACA and GNP into a long simulation box. Then, compressing to the densified model. Black, red, and white color spheres represent carbon, oxygen, hydrogen atoms, respectively.

The crosslinking process consisted of two main reactions as described in our previous work [100] but was executed until the crosslink conversion reached 80 percent or above. During the crosslinking process, every one hundred cycles, the crosslinked model was equilibrated with the NPT ensemble using isotropic pressure of 1 ATM. This equilibration step was carried out for 1 ns with 1 fs time steps. After the crosslinking process, the model was fully equilibrated for 2 ns with the NPT ensemble using anisotropic pressure of 1 atmosphere. As before, 1 fs time steps were used. The mass density was calculated every 1,000 time steps and the last ten mass densities were averaged to obtain the densities listed in Table 10. The crosslinked and equilibrated models shown in Figure 29 were used to determine the thermal conductivities as described below. Five different models of each system were

modeled for good statistical results. All crosslink percentages and mass densities are shown in Table 10.

Table 10 Crosslink percentage, mass density, and thermal conductivity of each system.

System	Crosslink percentage (%)	Mass density (g/cm ³)	Thermal conductivity (W/mK)	
			In-plane ($\kappa_x^{MD}, \kappa_y^{MD}$)	Out-of-plane (κ_z^{MD})
Neat CE	80.0 $\pm$ 0.0	1.199 $\pm$ 0.006	0.237 $\pm$ 0.016	
1GNP/CE	79.8 $\pm$ 0.4	1.243 $\pm$ 0.025	98.0 $\pm$ 11.6	0.192 $\pm$ 0.026
2GNP/CE	80.0 $\pm$ 0.0	1.330 $\pm$ 0.008	215.4 $\pm$ 12.5	0.184 $\pm$ 0.027
3GNP/CE	80.2 $\pm$ 0.4	1.401 $\pm$ 0.007	317.3 $\pm$ 17.3	0.171 $\pm$ 0.021
4GNP/CE	80.2 $\pm$ 0.4	1.498 $\pm$ 0.029	464.4 $\pm$ 37.8	0.151 $\pm$ 0.026

Figure 29 Representative crosslinked models of 1, 2, 3, and 4-layer GNP/CE after equilibration.

4.2.1.3 Thermal conductivity by EMD

All thermal conductivities were determined from five independent models of each system by using the EMD method. The thermal conductivity was calculated by the Green-Kubo approach

$$\kappa_x = \frac{1}{k_B T^2 V} \int_0^\infty \langle J_x(0) J_x(t) \rangle dt \quad (19)$$

where k_B is Boltzmann constant, T and V is temperature and volume of the system, respectively, $\langle \rangle$ denotes time average and $J_x(t)$ is heat flux in x direction at time t . The heat flux was calculated using the “compute heat/flux” command. Then, $\langle J_x(0) J_x(t) \rangle$, the heat flux autocorrelation function (HFACF) was obtained using the “fix ave/correlate” command. The HFACF was sampled every 5 time steps with 1 fs time steps for a total of 10,000 samples to let the HFACF decayed to zero. From Figure 30 to Figure 33 show the HFACF of 1, 2, 3, and 4-layer GNP/CE system, respectively.

Then, the HFACF was approximately integrated using the trapezoidal rule. The thermal conductivity (κ) was determined every 50,000 fs, and the simulation ran for 10 ns. The NVT ensemble was applied to maintain a temperature of 300 K, and the cut-off radius of pairwise interactions was specified at 10 Å. The last ten thermal conductivities for each direction were averaged to be used in the micromechanics calculations described in the follow section.

Figure 30 Normalized heat flux autocorrelation function for 1-layer GNP/CE system.

Figure 31. Normalized heat flux autocorrelation function for 2-layer GNP/CE system.

Figure 32. Normalized heat flux autocorrelation function for 3-layer GNP/CE system.

Figure 33. Normalized heat flux autocorrelation function for 4-layer GNP/CE system.

4.2.2 Micromechanics

Micromechanics analysis code based on the generalized method of cells (MAC/GMC) was implemented to determine the effective thermal conductivity of GNP/CE nanocomposites and GNP/CF/CE hybrid composites.

To determine the effective thermal conductivity of randomly oriented GNP/CE nanocomposites, all MD thermal conductivities (κ_x^{MD} , κ_y^{MD} , and κ_z^{MD}) were randomized by arithmetic averaging [102, 103] as shown in equation (20). MAC/GMC was then used to determine the randomized thermal conductivity (κ_{random}^{MD}) of GNP/CE nanocomposites of varying overall GNP concentrations (w_{GNP}^{RUC}) from 1 to 8 wt% by 1 wt% increments. A triply periodic repeating unit cell (RUC) with finite filler in a square packing array (ARCHID=1) was applied by assigning the bulk thermal conductivity of neat CE as the matrix region and assigning the effective thermal conductivity of randomized GNP/CE as the filler region. The RUC is shown in Figure 27.

$$\kappa_{random}^{MD} = \frac{\kappa_x^{MD} + \kappa_y^{MD} + \kappa_z^{MD}}{3} \quad (20)$$

$$w_{MD}^{RUC} = \frac{w_{GNP}^{RUC}}{w_{GNP}^{MD}} \quad (21)$$

$$v_{MD}^{RUC} = \frac{\rho_{CE} w_{MD}^{RUC}}{\rho_{GNP/CE} + w_{MD}^{RUC} (\rho_{CE} - \rho_{GNP/CE})} \quad (22)$$

MAC/GMC requires the volume fraction of the filler region which is given by the volume fraction of the GNP/CE MD cell in the RUC (v_{MD}^{RUC}). The mass fraction of GNP in the RUC (w_{GNP}^{RUC}) determines the mass fraction of the GNP/CE MD cell in the RUC (w_{MD}^{RUC}) and can be calculated by using equation (21). The mass fraction of GNP in each MD system is a

property of the MD model and is given in Table 10. Then, w_{GNP}^{RUC} was converted to v_{MD}^{RUC} by using equation (22). The mass densities of neat CE (ρ_{CE}) and GNP/CE ($\rho_{GNP/CE}$) systems are shown in Table 10. The aspect ratio of the filler region was set to 1 so that the effective thermal conductivity of GNP/CE was isotropic.

The effective thermal conductivities of GNP/CF/CE hybrid composites were also calculated by using MAC/GMC. This calculation used a circular fiber approximation RUC (rectangular pack or ‘Architecture 13’ as implemented in MAC/GMC). This RUC has 26×26 subcells where the 312 middle subcells were assigned to fiber region and the other subcells were the matrix region. AS4 carbon fiber properties were used in the fiber region, possessing axial and transverse thermal conductivities of 6.50 and 2.18 W/mK, respectively [73]. The matrix region was applied the thermal conductivity of randomized GNP/CE (from the preceding MAC/GMC calculation) as the matrix of the hybrid composite. The volume fraction of the carbon fiber was 0.56 for all calculations. The aspect ratio (R) of the RUC, that is, the ratio between the x_2 and x_3 directions (see Figure 27), was set to 1. Note that the mass fraction of GNP in the hybrid composites represented the amount of GNP in the matrix region only. The hybrid composite effective properties were determined in the axial (along the fiber) and transverse directions.

4.3 Experimental fabrication and testing*

For Neat CE samples [26]: A multi-part mold was coated with Mann Ease Release 300, then assembled and pre-heated in a vacuum oven at 100 °C. The amount of Resin needed was weighed into a beaker, the corresponding amount of Hardener was weighed into the same beaker. The beaker was then placed under a Ross High Sear Mixer (HSM-100 LSKI) with 2” dispersion blade. The mixture was mixed at 1000 rpm for 10 min, until the two parts were thoroughly mixed. The mixture was then degassed at 100 °C and 29 in Hg, alternating vacuum to avoid overflow, until no more bubbles appeared. The mixture was then poured into the pre-heated mold and degassed once more. The curing cycle used was

* This section was performed and wrote by Julie M Tomasi.

100 °C for 1 hour, then heated to 200 °C at 2°C/min then held at 200 °C for two hours. The oven was then turned off and the cured epoxy was allowed to cool in the oven to room temperature, ~1 °C/min cooling rate.

For 4 wt% GNP (Asbury Carbon TC307) in CE samples: A multi-part mold was coated with Mann Ease Release 300, then assembled and pre-heated in a vacuum oven at 100 °C. The amount of TC307 GNP needed was weighed into a beaker, the corresponding amount of Hardener was weighed into the same beaker. The beaker was then placed under a Ross High Sear Mixer (HSM-100 LSKI) with 2” dispersion blade. The mixture was mixed at 3000 rpm for 1 hour, then the mixture was placed in a Branson Sonicator CPX2800H operating at 40 kHz and sonicated for 1 hour. The needed amount of Resin (mixed Resin and Hardener) was added to the mixture, then mixed at 1000 rpm for 10 min, until well mixed. The mixture was then degassed at 100 °C and 29 in Hg, alternating vacuum to avoid overflow, until no more bubbles appeared. The mixture was then poured into the pre-heated mold and degassed once more. The curing cycle used was 100 °C for 1 hour, then heated to 200 °C at 2°C/min then held at 200 °C for two hours. The oven was then turned off and the cured epoxy was allowed to cool in the oven to room temperature, ~1 °C/min cooling rate.

Through-plane thermal conductivity was measured using a Holometrix Model TCA-300 Thermal Conductivity Analyzer, which follows ASTM F433 [79] guarded heat flow meter method. The through-plane thermal conductivity of a 3.2 mm thick, 5 cm diameter disc-shaped test specimen was measured at 55 °C. Table 11 shows the through-plane thermal conductivity for neat CE and 4 wt% GNP/CE at 55 °C. The thermal conductivity increases slightly for the 4 wt% GNP/CE as compared to the neat CE.

Table 11 Thermal conductivity of neat ce and 4 wt% gnp/ce from experiment.

Samples	Number of Samples	Thermal Conductivity (W/mK)
Neat CE	4	0.150 ± 0.002
4 wt%GNP/CE	5	0.178 ± 0.002

4.4 Results

All GNP/CE molecular models have consistent density profiles along the z-direction (perpendicular to GNP) as shown from Figure 34 to Figure 37. The middle peaks represent the GNP layers and the plateaus on both sides indicate the cured CE regions. The crosslink percentage of the matrix in all nanocomposite models is about 80%. The vertical dashed lines were drawn as boundaries to distinguish the GNP and matrix regions. These boundaries lines were determined by the van der Waals's radius of the carbon atoms in GNP which is 3.55 Å according to the OPLS-AA force field. The GNP volume fraction of the MD system can be calculated from the ratio of the length of the GNP region to the overall length of the simulation box in the z-direction, since the x-y area is the same throughout the simulation box. The mass densities of all MD models are shown in Table 10. The neat CE models have an average mass density equal to 1.199 g/cm³. For the GNP/CE models, the average mass densities are equal to 1.243, 1.330, 1.401, and 1.498 g/cm³ for 1, 2, 3, and 4 layer(s) of GNP nanocomposite models, respectively.

Figure 34. Plot of density profiles of the equilibrated models of 1-layer GNP/CE system.

Figure 35. Plot of density profiles of the equilibrated models of 2-layer GPN/CE system.

Figure 36. Plot of density profiles of the equilibrated models of 3-layer GNP/CE system.

Figure 37. Plot of density profiles of the equilibrated models of 4-layer GNP/CE system.

From Table 10, the in-plane (parallel) thermal conductivities (prior to randomization) obtained from MD of CE nanocomposites with 1, 2, 3 and 4-layer GNP are equal to 98.0, 215.4, 317.3, and 464.4 W/mK with 0.151, 0.287, 0.408, and 0.517 of GNP mass fraction, respectively. The GNP volume fractions of these four systems are equal to 0.085, 0.172, 0.258, and 0.349, respectively. The out-of-plane (perpendicular) thermal conductivities are equal to 0.192, 0.184, 0.171, and 0.151 W/mK, respectively, which decrease with more layers of GNP. However, the overall thermal conductivities will primarily be affected by the in-plane conductivities.

In this chapter, the normalized thermal conductivity was calculated as the ratio between the effective thermal conductivity of the models with and without GNP. The normalized thermal conductivity was used to determine how GNPs improve the thermal conductivity of composite materials. In Figure 38, the normalized thermal conductivity of randomized 1GNP/CE (blue line) is the highest compared to the other systems at the same GNP concentrations. It is clear that better GNP dispersion gives higher thermal conductivity. At 1 wt% GNP of 1GNP/CE, the normalized thermal conductivity of our prediction and the experimental measurement of GNP/Epoxy from Kostagiannakopoulou et al. [17] are equal

to 1.11, and 1.10, respectively, which shows good agreement. The model predicts a lower value when compared with the GNP/Epoxy nanocomposite specimen from Yang et al. [28] which resulted in a normalized conductivity of 1.24 for 1 wt% GNP. The normalized thermal conductivity of the 3 wt% GNP specimen of Kostagiannakopoulou et al. [17] is equal to 1.41, comparing well with the model (1.46). However, the 5 wt% 1GNP/CE model is 20% higher than the experimental specimen. While the 1GNP/CE model and Kostagiannakopoulou et al. data agree well for low GNP concentration, the model diverges from the experimental measurement for high wt% GNP. The observed discrepancy is likely due to the increased difficulty of achieving good GNP dispersion at greater loadings. Therefore, we estimate that the specimen from Kostagiannakopoulou et al. can theoretically be further increased in conductivity by 20% with improved dispersion.

Figure 38. Plot of normalized thermal conductivity of randomized GNP/CE models as function of GNP mass fraction compared with experiments [11, 14, 17, 28].

Similar behavior is also observed when comparing the 1GNP/CE model with the values of GNP/Epoxy obtained by Ganguli et al. The normalized thermal conductivities of 1CE/GNP at 2 wt% and 4 wt% GNP are 1.26 and 1.71, respectively, and are in good agreement with exfoliated graphite specimens from Ganguli et al. [14] yielding values of 1.33 and 1.64, respectively. At 8 wt% GNP, 1GNP/CE has a higher normalized thermal conductivity than the same GNP mass fraction specimen of Ganguli et al. [14]. For this loading, the predicted and experimental values are 3.63 and 2.96, respectively. This shows that the experimental specimen likely has GNP agglomeration for high GNP concentrations. Ganguli et al. also observed that there was the optimum GNP concentration before the GNP re-agglomerated when having the higher GNP concentration. In this research, we experimentally measured the normalized thermal conductivity of 4 wt% GNP/CE to be 1.19. Our experimental GNP/CE specimen falls between the double-layer GNP and triple-layer GNP models. While there is probably significant variation in the number of GNP layers in the experimental specimen, our multiscale model suggests that the GNP is effectively two-to-three layers thick. The exfoliated GNP/Epoxy specimens from Debelak and Lafdi resulted in normalized thermal conductivities lower than the 4GNP/CE model for both 0.5% and 4 wt% GNP, meaning that the specimens could have more than four layers of exfoliated graphite.

The effective thermal conductivities of GNP/CF/CE hybrid composite were also normalized with the CF/CE composite (without GNP) for both the axial and transverse directions (shown in Figure 39 and Figure 40). Both plots show that improving the GNP dispersion results in higher thermal conductivity. The axial thermal conductivity of the GNP/CF/CE hybrid composite increases less than 8% for 8 wt% of single layer GNP and less than 2% for 8 wt% of non-single layer GNP. By doping GNP into the composites, the thermal conductivity hardly increases in the fiber direction because the axial thermal conductivity of the carbon fiber dominates this property.

Figure 39. Plot of normalized axial thermal conductivity of GNP/CF/CE hybrid composites models.

The transverse thermal conductivity of the GNP/CF/CE hybrid composites model is greatly improved by doping GNP. At 8 wt% single-layer GNP, the transverse thermal conductivity is predicted to increase by 132% when compared with no GNP reinforcement. For the same GNP mass fraction of 2, 3, and 4-layer GNP, the hybrid composite transverse thermal conductivities can be raised up to 47%, 27%, and 18% when compared with the absence of GNP.

In Figure 40, the results from the multiscale model of GNP/CF/CE are compared with the experimental values of GNP/CF/Epoxy. The normalized thermal conductivity through the composite plane (transverse) measured by Zhang et al. [31] are equal to 1.11 and 1.45 for 0.5% and 4 wt%, respectively, of pristine graphene (to the epoxy matrix). For 0.5 wt% single-layer GNP in the GNP/CF/CE hybrid composites, the model underestimates the conductivity, but the 4 wt% single-layer GNP model estimated the normalized transverse thermal conductivity to be 1.47, which is very close to the experiment value. These specimens are conjectured to have well-dispersed pristine graphene.

Figure 40. Plot of normalized transverse thermal conductivity of GNP/CF/CE hybrid composites models compared with experiments [13, 16, 18, 31].

Fan et al. [13] examined the transverse thermal conductivity of GNP/CF/Epoxy hybrid composites with 1 wt% of GNP (to the overall composite with 55% of carbon fiber or 2.9 wt% GNP relative to matrix) equal to 1.13 times the composites without GNP. By comparison with our multiscale model, this experimental specimen could have effectively double-layered GNP. Additional GNP/CF/epoxy hybrid composites specimens were investigated by Kandare et al. [16] with 1 vol% of GNP (to the overall composite with 45 vol% of carbon fiber). The hybrid composite specimen resulted in an increase of 9% in the transverse thermal conductivity when compared with no GNP reinforcement. By comparison with our model, this hybrid composite could have effectively triple layers of GNP. Another experimental study was conducted by Li et al. [18] where GNP/CF/epoxy hybrid composites were created with 2% and 5 wt% of GNP (to the epoxy matrix). Their transverse thermal conductivities improved 8% and 50% compared to the carbon fiber reinforced plastic without GNP. The 2 wt% GNP specimen appears to possibly be double-

layered GNP, and the 5 wt% GNP specimen falls between our single- and double-layered GNP models.

The GNP can improve the thermal conductivity in the transverse direction because the transverse thermal conductivity of carbon fiber is lower than the axial direction and the matrix usually plays the dominant role in the transverse properties. Consequentially, if the thermal conductivity of the matrix increases, the effective thermal conductivity of hybrid composite also improves. Moreover, the improvement of thermal conductivity in transverse direction actually improves on two axes in Cartesian coordinate system.

4.5 Conclusions

A multiscale modeling approach was developed to predict the thermal conductivity of CE-matrix hybrid composites using EMD with OPLS-AA force field and micromechanics. Our method provides realistic results for the thermal conductivity of GNP/CE nanocomposites and GNP/CF/CE hybrid composites when compared with experiments. The perfectly dispersed GNP model gives the highest thermal conductivity of our GNP/CE systems. For low GNP concentrations, several experimental results closely match the perfectly dispersed model, but none of these experimental specimens were observed to reach the ideal model for 5 wt% GNP or greater. Thus, we suspect that some agglomeration occurs for these highly loaded specimens and improvements in thermal conductivity can theoretically be achieved by pursuing even better dispersion. Our results provide a guide for other researchers to assess the effective dispersion of GNP/CE and GNP/CF/CE experimental samples as we have demonstrated here. For GNP/CF/CE hybrid composites, the transverse thermal conductivity is predicted to increase up to 132% for 8 wt% GNP (compared to no GNP) given ideal dispersion.

CHAPTER 5 MULTISCALE MODELING: THERMAL CONDUCTIVITY OF CARBOXYL (-COOH) FUNCTIONALIZED GRAPHENE NANOPLATELET/CYCLOALIPHATIC EPOXY NANOCOMPOSITE

5.1.1 Introduction

The thermal transport is extremely important to the advance applications such as the electronic industry, spacecraft, and aircraft. This is because the heat is always generated during the operation so the heat dissipation from the heat source is required to let those applications work effectively and safely. As the superior thermal conductivity of pristine graphene, the experimental value can be above 5,000 W/mK at the room temperature [5, 6]. The graphene nanoplatelet (GNP) with perfect dispersion which can improve the thermal conductivity of epoxy is desired. One of the technique that can facilitate the dispersion of GNP is the functionalization [104].

In this chapter, Cycloaliphatic Epoxy (CE) and Anhydride Curing Agent (ACA) are both used to study the effect of the functionalized GNP. Since curing mechanism between CE and ACA has a carboxyl and hydroxyl groups as reactive groups, either one of these groups is selected to be the functionalized group. Recently, MD work [105] shows that the functionalized group can reduce the interfacial resistance between graphene and paraffin. The out-of-plane thermal conductivity can be potentially increased by adding the functionalized groups to GNP. Moreover, this study also shows that the carboxyl group is better than the hydroxyl in term of the interfacial resistant reduction. Therefore, the carboxyl group is focused to study the effect of GNP functionalization (fGNP) on thermal conductivity of fGNP/CE composites.

The objective of this study is to understand how the covalently functionalization between GNP and epoxy affect the thermal conductivity. A single-layer GNP is focused in this study and functionalized with carboxyl group. Multiscale modeling is used to study the fGNP/CF/CE composites model including Molecular Dynamics (MD) modeling and micromechanics. The thermal conductivity of fGNP/crosslinked CE nanocomposites is determined by Equilibrium MD with different amount of functionalization. The thermal conductivities are homogenized by arithmetic average and scaled the GNP mass fraction by micromechanics.

5.2 Computational Details

The carboxyl fGNP models were prepared by using MD. Then, each fGNP model was combined with neat CE system to determine the thermal conductivity of fGNP/CE nanocomposites by using EMD. At microscale, the thermal conductivity of nanocomposite was randomized by arithmetic average and scaled the GNP mass fraction by using micromechanical modeling. All details of each step are given as following.

5.2.1 MD modeling

5.2.1.1 Functionalized Graphene MD Model

The single-layer graphene with 576 carbon atoms was prepared as shown in Figure 41 by using “lattice” command in LAMMPS. For the functional group, the carboxyl groups were separately created with two different formations as shown in Figure 42. These representative carboxyl groups were used to randomly add above and below the GNP layer by using Python script. The script generated 100 small boxes spanned on the top and bottom of GNP simulation box by offsetting 4 Å from the edge of GNP simulation box. Then, each carboxyl group was put into the small box with the same number of groups on each side. There were two different amount of carboxyl groups: 5 and 10 carboxyl groups on each side which were called 5-5fGNP and 10-10fGNP, respectively as shown in Figure 43.

Figure 41 A single-layer GNP model for preparing fGNP model.

Figure 42 The molecular structures of carboxyl groups for placing above (left) and below (right) GNP, respectively. Red: oxygen, gray: carbon, white: hydrogen.

Figure 43 Representative pre-functionalized GNP and carboxyl groups models for 5-5fGNP/CE (left) and 10-10GNP/CE (right) systems.

The combined fGNP model was created the bond between carbon atoms from a carboxyl and GNP by using “fix bond/create” command on LAMMPS. The atom type of functionalized carbon on GNP was changed from sp^2 to be sp^3 type. All angles and dihedrals were updated by using Python script. The bonded fGNP models were minimized energy using “minimize” command with conjugate gradient (CG) algorithm by setting $10e-4$ energy tolerance and then dynamically equilibrated using NPT ensemble for 300 ps with 1 fs time steps at 300K. Figure 44 and Figure 45 shows the molecular structure of equilibrated 5-5fGNP and 10-10fGNP models, respectively.

Figure 44 Molecular structure of 5-5fGNP.

Figure 45 Molecular structure of 10-10fGNP.

Figure 46 The ratio between defected carbon (SP³) and GNP carbon (SP²) on fGNP

Model	SP ³ /SP ² of carbon (%)
5-5fGNP/CE	1.74
10-10fGNP/CE	3.47

5.2.1.2 fGNP/CE nanocomposites MD Model

The nanocomposite model of fGNP/CE includes fGNP model as the nanoparticle shown in Figure 44 and Figure 45 and CE system as the matrix. Epoxy Cyclohexyl Methyl 3,4 Epoxy Cyclohexyl Carboxylate (EEC) and 4, 7-Methanoisobenzofuran-1, 3-dione, 3a, 7, 7a-tetrahydromethyl or Anhydride Curing Agent (ACA) are the resin and hardener of CE matrix, respectively. In this MD model, the modified ACA also included to initiate the curing mechanism. Molar ratio of EEC : ACA : modified ACA was equal to 7 : 13 : 1 with total 5,373 CE atoms.

All fGNP, EEC, ACA, and modified ACA molecules were combined into a long box which normal direction of fGNP was in z direction and the plane stayed in middle of simulation box. The box was compressed by using “fix deform” command in LAMMPS and NVT ensemble was used to control the temperature at 300K. The final dimensions were 38.69, 37.70, 36.18 Å in x, y, z direction, respectively. This densification ran for total 5.2 ns with 1 fs time steps using the stepwise approach shown in Table 9. Lennard-Jones cutoff radius was 10 Å. Density profile on each direction was determine at the end of simulation to ensure that the density profiles of system were uniform. Five models of 5-5fGNP/CE and 10-10fGNP/CE models were created to obtain the good-statistical results.

The crosslinking process had two part. The first part was to establish the crosslinked bond between carboxyl group on fGNP and epoxide group on EEC similar to the esterification reaction. The initial bond between oxygen atom on carboxyl group and carbon atom on epoxide group was created by using “fix bond/create” command with 7 Å as minimum

distance in LAMMPS. The simulation performed by NVT ensemble for 200 fs with 0.1 fs time steps at 300K. Non-bonded interaction was Lennard-Jones with 15 Å cutoff radius to prevent any high energy atom moves away. Then, the related bonds were updated by using Python script. All angle and dihedral were also reassigned by using general angle-dihedral Python script. The hydroxyl groups were appeared after the reaction.

The second part was the crosslinking process in CE matrix. There were two reactions that were esterification and anhydride ring opening reaction. For the esterification, the carboxyl groups on modified ACA molecules were first reacted with the epoxide groups on EEC molecules by using “fix bond create” command with similar control as mentioned above. The relative bond and VdW configuration was updated by Python script giving hydroxyl groups. Their angle and dihedral information was reassigned by general angle-dihedral Python script. The hydroxyl groups from the functionalization and the esterification were consumed to open anhydride ring on ACA molecules.

For the anhydride ring opening reaction, the initial bonds between hydrogen atom and oxygen atom were created by using “fix bond/create” command which those atoms were from hydroxyl group and anhydride ring, respectively. The bonds were built with the same previous bond-created setup. Another bonds related to the initial bond were generated by running Python script. The relative bonds on the carboxyl groups and the anhydride rings were assigned to be deleted within the same Python script. For relative angle and dihedral, the general angle-dihedral Python script updated according to the new bonds. This reaction exposed the carboxyl groups which were continuously used in the esterification. Both reactions alternately performed till 80% of the crosslink percentage was achieved.

After the crosslinking process, the crosslinked models were equilibrated by using NPT ensemble with at 1 atm and 300 K. The barostat was chosen to be “aniso” type. Lennard-Jones potential was used as non-bonded interaction with 10 Å cutoff radius. The mass density of fGNP/CE model was averaged for last 12 ps of simulation. The density profile along out-of-plane direction of fGNP was determined with 1,000 flattened slabs using “fix ave/chunk” command. The density profile was determined by averaging the mass density

each slab every 1 ps using 10 input with interval of 100 time steps. The simulations were performed along 2 ns with 1 fs time steps. The average mass densities and GNP volume fractions of both systems are shown in Table 12. The equilibrated 5-5fGNP/CE and 10-10fGNP/CE models shown as Figure 47 and Figure 48 were ready to determine the thermal conductivity.

Table 12 Density, GNP volume fraction, and thermal conductivity of fGNP/CE, GNP/CE and neat CE at 300 K.

Model	GNP volume fraction	Density (g/cm ³)	Thermal Conductivity (W/mK)	
			In-plane	Out-of-plane
neat CE	0.000	1.199 ± 0.006	0.237 ± 0.016	
1GNP/CE	0.085	1.243 ± 0.025	98.019 ± 11.560	0.192 ± 0.026
5-5fGNP/CE	0.086	1.282 ± 0.009	6.662 ± 0.938	0.221 ± 0.031
10-10fGNP/CE	0.086	1.293 ± 0.017	4.574 ± 1.041	0.218 ± 0.020

Figure 47 Representative crosslinked model of 5-5fGNP/CE after equilibration.

Figure 48 Representative crosslinked model of 10-10fGNP/CE after equilibration.

5.2.1.3 Thermal conductivity by EMD

EMD method based on Green-Kubo approach was used to find the thermal conductivity of fGNP/CE nanocomposites. NVT ensemble perform for 10 ps with 1 fs time steps to obtain system temperature at 300 K. The heat flux was then computed from kinetic energy, potential energy, and stress by using “compute stress/atom”.

$$\kappa_x = \frac{1}{k_B T^2 V} \int_0^\infty \langle J_x(0) J_x(t) \rangle dt \quad (23)$$

The heat flux (J) was identified main signal by using autocorrelation function to conceal the noise in heat flux data. The autocorrelation function was performed by using “fix ave/correlate” command with “auto” option. This command auto correlated the heat flux total 10,000 inputs with interval of 5 time steps and total correlation time was 50 ps. This heat flux autocorrelation function (HFACF) was integrated by using trapezoidal rule. The thermal conductivity was calculated form equation (23) which the integral term was divided by Boltzmann constant, Square of temperature, and system volume. The thermal conductivities of 5-5fGNP/CE and 10-10fGNP/CE models are shown in Table 12.

5.2.2 Micromechanics

Micromechanics method of fGNP/CE composites was similar to the micromechanics calculation of GNP/CE composites in Chapter 4. A $2 \times 2 \times 2$ Repeating Unit Cell (RUC) was used in the same manner. A subcell was applied the randomization fGNP/CE's thermal conductivity which averaged the thermal conductivities in all axes from MD models shown in Table 12. The thermal conductivity of neat CE was added into the others seven subcells in the RUC. The aspect ratio of 1 was chosen in this calculation.

5.3 Results

Table 13 shows the results of the covalently functionalization between fGNP with carboxyl group and CE matrix for two levels of functionalization. The 5-5fGNP/CE and 10-10fGNP/CE systems can potentially have 1.7 and 3.5% of functionalization, respectively. During the functionalization process between carboxyl groups on fGNP and epoxide groups on EEC, the 5-5fGNP/CE models are 100% of potential functionalization but the 10-10 fGNP/CE models are about 90% of potential functionalization. Therefore, the actual functionalization of 5-5fGNP/CE and 10-10fGNP/CE is 1.7 and 3.1% of functionalization.

Table 13 Functionality and crosslink density of fGNP/CE nanocomposites models.

Model	fGNP/CE			Crosslink density in CE matrix (%)
	Potential functionality (%)	Percentage of covalent bond between fGNP and CE (%)	Actual functionality (%)	
5-5fGNP/CE	1.7	100	1.7	72
10-10fGNP/CE	3.5	90	3.1	67

During the crosslink process, some of epoxide groups were already consumed by the functionalization. The crosslink densities of CE matrix in 5-5fGNP/CE and 10-10fGNP/CE systems are shown in Table 13 which are lower than the crosslink of the CE matrix in

1GNP/CE and neat CE models. Figure 25 shows that the thermal conductivity by the EMD method has similar values for the systems with 60 – 90% crosslink.

Figure 49 shows that the density profiles of 5-5fGNP/CE models have more fluctuation of the CE matrix regions compared to the density profiles of 1GNP/CE models shown in Figure 34. This is because the fGNP surfaces are bumpy unlike the pristine graphene surface due to the inclusion of functionalized groups. Figure 49 also shows the planes of fGNP are still flat and the density of fGNP is relatively uniform when comparing each model.

Figure 49 The plot of density profiles of 5-5fGNP/CE models along z axis.

For the 10-10fGNP/CE system, the density fluctuations are also found in the CE matrix regions shown in Figure 50. The density at interphase regions of this system have more oscillated than the 5-5fGNP/CE system because 10-10fGNP/CE system has more covalently bonded at the interphase region. Moreover, Figure 50 also shows that each density profile of fGNP is different from the others. The more covalently bonded functionalization can affect the plane of fGNP. The 3rd model of 10-10fGNP/CE has two peaks of density profile in the fGNP region which is so different from the other model.

Figure 50 The plot of density profiles of 10-10fGNP/CE models along z axis.

The front view of the 3rd fGNP/CE model is shown in Figure 51 which the fGNP is bent by the functionalized bonds. A particular cluster of carboxyl groups (red circle) on the bottom surface of fGNP shown in Figure 52 has effect on the shape of fGNP. On the top surface, the carboxyl group are located as surrounding the cluster. After the equilibration, these carboxyl groups which covalently bonded to the CE matrix are pulled by the expanding of CE matrix. However, the thermal conductivity of this particular model is relatively close to the other models.

Figure 51 The 3rd crosslinked model of 10-10fGNP/CE.

Figure 52 The cluster of functional groups shown on the top (left) and bottom (right) surfaces of fGNP of the 3rd 10-10fGNP/CE model.

The thermal conductivities of 5-5fGNP/CE and 10-10fGNP/CE models are shown in Table 12. The in-plane thermal conductivities of these two systems are significant lower than the thermal conductivity of 1GNP/CE systems. The phonon can easily travel through the crystal structure like graphene, however, the inclusion of functionalized groups disturbs the sp^2 structure. Consequently, the more of defects on GNP, the lower in-plane thermal conductivity of nanocomposites can be obtained. The out-of-plane thermal conductivities of both fGNP/CE systems are higher than the 1GNP/CE system but they are still lower than neat CE system.

Figure 53 The plot of normalized thermal conductivity of functionalized and pristine GNP/CE as the function of GNP mass fraction.

Figure 53 shows the thermal conductivities of fGNP/CE composite models from MAC/GMC as the function of GNP mass fraction. The plot shows the normalized thermal conductivities of 5-5fGNP/CE and 10-10fGNP/CE systems compared with the pristine GNP/CE models. The thermal conductivities (solid lines) of GNP/CE with four different levels of GNP dispersion are taken from Figure 38. The thermal conductivities (Dashed blue lines) of fGNP/CE are lower than the thermal conductivity (Solid blue line) of single-layered pristine GNP/CE. The increasing of functionalization in fGNP/CE system

decreases the thermal conductivity at the same level of GNP dispersion. However, both fGNP/CE systems have the higher thermal conductivities than the pristine GNP/CE system having more than one layer of GNP. The functionalization on GNP [106] can provide the better GNP dispersion to the composite. This effect can be also found in the single-wall carbon nanotube (CNT)/epoxy composites [107] which the functionalization improves CNT dispersion in epoxy composites.

5.4 Conclusions

The functionalized GNP/CE models can be established by using MD modeling and the EMD approach is able to predict the thermal conductivity fGNP/CE nanocomposites. The functionalization on GNP significantly decreases the in-plane thermal conductivity of GNP/CE nanocomposites. The out-of-plane thermal conductivity slightly increases due to the functionalization but no greater the thermal conductivity of neat CE.

Micromechanical calculation is capable to determine the thermal conductivity of fGNP/CE composites with different GNP mass fractions. The effective thermal conductivity of fGNP/CE decreases with increased the functionalized percentage. One of important aspect of functionalized GNP is to improve GNP dispersion in the composites. The thermal conductivities of fGNP/CE models are all higher than the thermal conductivities of 2-, 3-, and 4-layered GNP/CE models. Additionally, the aspect ratio of GNP and thermal pathway are still needed to be further investigated.

CHAPTER 6 MULTISCALE MODELING: COEFFICIENT OF LINEAR THERMAL EXPANSION OF CARBON FIBER/GRAPHENE NANOPATELET/EPON862 HYBRID COMPOSITES

6.1 Introduction

Carbon fiber (CF) composites with EPON862 matrix have been used in the structural components of aircraft and spacecraft. These composites are light, strong and chemically resistant. However, the stiffness of the composites in the transverse direction is weak due to the characteristic of matrix (EPON862 system). Graphene nanoplatelet (GNP) has been used as the additive to improve the mechanical properties of the matrix.

The prediction of mechanical properties of GNP/EPON862 nanocomposites. was studied by Hadden et al. (2015) [36]. Molecular dynamics (MD) was used along with OPLS all atom force field which the resulting elastic properties are shown in Table 14. Four different levels of GNP dispersion were investigated which a single layer GNP/EPON862 was determined as the perfectly dispersed system.

Table 14 Elastic properties of GNP/EPON862 models from Hadden et al. [36].

GNP layers	GNP volume fraction	E_x	E_y	E_z	G_{xy}	G_{xz}	G_{yz}	V_{xy}	V_{xz}	V_{yz}	V_{yx}	V_{zx}	V_{zy}
1	0.111	93.4	94.8	2.432	0.243	0.001	0.001	0.13	0.46	0.471	0.158	0.109	0.025
2	0.187	174.6	172.5	2.731	0.424	0.001	0.001	0.168	0.437	0.524	0.153	0.056	0.015
3	0.271	239.4	238.3	3.005	0.582	0.001	0.001	0.152	0.44	0.446	0.151	0.01	0.034
4	0.33	293.1	295.5	3.251	0.725	0.001	0.001	0.159	0.455	0.452	0.156	0.011	0.009

The coefficient of linear thermal expansion (CLTE) is another crucial material property to indicate how the size of system changes along each Cartesian direction when the

temperature increases or decreases. The CLTEs of GNP/EPON862 have not yet been studied by MD modeling. In this chapter, the CLTEs of GNP/EPON862 models were determined by MD. The CLTEs were homogenized for GNP/EPON862 composites and CF/GNP/EPON862 hybrid composites by micromechanics.

6.2 Computational Details

The work flow to determine effective CLTEs of CF/GNP/EPON862 hybrid composites is shown in Schematic 2. There were two main parts including MD modeling and micromechanics. For MD modeling, the MD models of GNP/EPON862 obtained from C. Hadden et al. (2015) [36] were determined the CLTE. For micromechanics, the effective CLTEs of GNP/EPON862 composites and CF/GNP/EPON862 hybrid composites were calculated including the GNP randomization.

Schematic 2 The flow chart for calculating the effective coefficient of thermal expansion of GNP/CF/EPON862.

6.2.1 MD modeling

All four levels of dispersion GNP/EPON862 modeled by Hadden et al. [36] were used for this analysis. The 80% crosslinking models were selected as most realistic. The models

were equilibrated by using NPT ensemble with the “aniso” type of barostat (as implemented in LAMMPS) at 1 atmosphere and 300K. The equilibration ran for 2 ns with 1 fs timesteps. The cut-off radius for airwise interactions was set at 10 angstroms. All equilibrated models were prepared by reducing the temperature to 173K in the NPT ensemble with the aniso type of barostat set at 1 atmosphere. This preparation ran for 500 ps with 1 fs timesteps. Subsequently, simulations were performed with two different methods (heating-up and cooling-down) to determine the CLTE. The heating-up method continued from the preparation step by heating from 173K up to 800K using the NPT ensemble with aniso at 1 atmosphere for 5 ns with 1 fs timesteps. The cooling-down method was continuously applied after the heating up method by decreasing the temperature from 800K to 173 K with the same settings and simulation time. The temperatures and box lengths on each direction were individually averaged every 2 ps and exported to a log file. The CLTE was calculated using,

$$\alpha = \frac{1}{\delta T} \frac{\delta L}{L} = \frac{1}{L} \frac{\delta L}{\delta T} \quad (24)$$

where L is the length of box and T is the temperature of the system. The CLTEs of each system are shown in Table 15 on x, y, and z axes.

Table 15 Predicted CLTEs of GNP/EPON862 from MD simulations.

GNP layers	α_x (ppm/°C)	α_y (ppm/°C)	α_z (ppm/°C)	α_r (ppm/°C)
1	-7.343	-9.344	260.015	9.955
2	-7.253	-8.306	234.41	1.685
3	-7.943	-6.482	210.944	-1.526
4	-7.449	-7.887	207.528	-4.591

6.2.2 Micromechanics

The CLTEs of GNP/epoxy models were randomized by using the equation by Craft et al. [108].

$$\alpha_r = \frac{[E_{11} + 4\nu_{12}(1 + \nu_{12})K_{23}]\alpha_1 + 4(1 + \nu_{12})K_{23}\alpha_2}{E_{11} + 4\nu_{12}(1 + \nu_{12})K_{23}} \quad (25)$$

The elastic properties in Equation (25) were taken from Table 14. The bulk modulus is defined as

$$K_{23} = \frac{1}{2} \left[\frac{2}{E_{22}} - \frac{2\nu_{12}^2}{E_{11}} - \frac{1}{2G_{23}} \right]^{-1} \quad (26)$$

where G_{23} is transverse shear modulus which can be calculated by

$$G_{23} = \frac{E_{22}}{2(1 + \nu_{23})} \quad (27)$$

The randomized CLTE values are given in Table 15. The mechanical properties were also randomized by using Christensen & Walls equation [109]

$$E_r = \frac{[E_{11} + (4\nu_{12}^2 + 8\nu_{12} + 4)K_{23}][E_{11} + (4\nu_{12}^2 - 4\nu_{12} + 1)K_{23} + 6(G_{12} + G_{23})]}{3[2E_{11} + (8\nu_{12}^2 + 12\nu_{12} + 7)K_{23} + 2(G_{12} + G_{23})]} \quad (28)$$

$$\nu_r = \frac{E_{11} + (4\nu_{12}^2 + 16\nu_{12} + 6)K_{23} - 4(G_{12} + G_{23})}{4E_{11} + (16\nu_{12}^2 + 24\nu_{12} + 14)K_{23} + 4(G_{12} + G_{23})} \quad (29)$$

where E_{11} , ν_1 , and G_{12} were the elastic properties given in Table 14, K_{23} and G_{23} were calculated using Equation (26) and (27), respectively. The randomized elastic properties of GNP/EPON862 MD model are shown in Table 16.

Table 16 The randomized elastic moduli and Poisson's ratios of GNP/EPON862 MD models.

GNP layers	E_r (GPa)	ν_r
1	55.338	0.304
2	93.247	0.246
3	123.939	0.213
4	149.264	0.194

MAC/GMC [75] was used to determine the CLTE of the homogenized GNP/epoxy composite. A triply periodic 2x2x2 RUC (cubic packing array), shown in Figure 6 was employed, with the aspect ratio equal to 1.

Figure 54 The representative simple cubic packing RUC.

The randomized CLTE of GNP/epoxy from Table 15 was applied as the inclusion region. The elastic properties of a system from Table 16 containing GNP/epoxy at completely random orientations were put into the same region. The elastic modulus [$E = 2.72$ GPa] and properties Poisson's ratio [$\nu=0.43$] of the pure epoxy are from Klimek-McDonald D [80] and Little et al. [110], respectively. The shear modulus was calculated by Equation (30) equal to 0.951 GPa and the CLTE [$\alpha=86$ ppm/ $^{\circ}\text{C}$] of the pure epoxy was taken from the work of Bandyopadhyay et al. [46].

$$G = \frac{E}{2(1 + \nu)} \quad (30)$$

The volume fraction of the subcell containing the properties from the randomization of the MD results was calculated using Equation (31) to provide a consistent overall GNP volume fraction in the RUC.

$$v_{MD}^{RUC} = \frac{v_{GNP}^{RUC}}{v_{GNP}^{MD}} \quad (31)$$

The total GNP volume fractions in RUC (v_{GNP}^{RUC}) were specified from 0.01 to 0.10 with 0.005 of increments. The GNP volume fraction in MD was used from Table 14. The randomization of the GNP/epoxy occurred immediately after the MD calculations, and the randomized MD CLTEs were used in the micromechanics model of the GNP/Epoxy RUC. This workflow is analogous to that demonstrated by Hadden et al. [36] The error introduced when calculating the effective CLTE for the GNP/epoxy composite should be minimal because these properties are linear and mainly a function of the volume fraction of the constituents, and the overall orientation distribution of the inclusion.

The CLTEs of GNP/CF/EPON862 hybrid composite (lamina) model were calculated by using MAC/GMC as well. The 26×26 Circular Fiber Approximation, Rectangular Pack RUC (ARCHID=13) was employed to determine both axial and transverse CLTEs. The 312 middle subcells of this RUC are the fiber region which the materials properties of carbon fiber were added as shown in Table 17. The axial (α_A) and transverse (α_T) CLTEs of carbon fiber were from [111]. The volume fraction of carbon fiber was fixed at 56%. The materials properties of randomized GNP/EPON862 were applied to the reset of subcells as the matrix region. All four different systems were studied in this hybrid composites. The volume fractions of GNP were also indicated in this region which were 0.01 to 0.10 with 0.005 increments.

Table 17 Elastic properties and CLTEs of carbon fiber.

E_A (GPa)	E_T (GPa)	G_A (GPa)	ν_A	ν_T	α_A (ppm/°C)	α_T (ppm/°C)
231	9.6	112	0.30	0.07	-0.84	7.8

6.3 Results

The calculated CLTEs are shown in Table 15. They were determined by averaging the results from the heating and cooling methods. The in-plane CLTEs (x and y directions in Figure 5) were all negative values meaning that the in-plane dimension of box shrank at the higher temperature in those directions. Those contractions resulted the box expanded in z direction and the out-of-plane CLTE (z direction) was very high due to Poisson's contraction concept. The elastic properties used in Equation (25) were taken from Table 14, and the randomized CLTE values are given in Table 15.

Figure 55 The plot of normalized CLTEs of GNP/EPON862 models as the function of GNP volume fraction compared with the experimental values [112].

Subsequent to randomization, the CLTE of the GNP/EPON862 system is calculated by homogenizing a 2x2x2 RUC with MAC/GMC to account for the appropriate volume fraction of GNP. The volume fraction of the (inclusion) subcell which utilized the GNP/EPON862 CLTEs predicted using MD was calculated for overall GNP volume

fractions ranging from 0% to 10% and different dispersion levels. The resulting normalized CLTEs which the ratio of CLTEs between GNP/EPON862 and neat EPON862 systems are shown in Figure 55. The plot shows that the different levels of GNP dispersion strongly affects to the CLTE. The perfectly dispersed GNP system is most decreased CLTE. The normalized CLTEs of graphene oxide (GO)/EPON862 specimens from experiment by Wang et al. [112] were also shown in Figure 55. The experimental value was approximately equivalent to the single GNP/EPON862 model. This is because the oxides on graphene facilitate the GNP exfoliation. We recognize that the GNP aspect ratio of this calculation was fix as the constant.

Figure 56 The plot of coefficient of thermal expansion along fiber direction as the function of GNP volume fraction.

Figure 56 and Figure 57 show the axial and transverse CLTEs of GNP/CF/EPON862 lamina calculated using MAC/GMC, respectively. The CLTE properties of matrix subcells were from the representative of homogenized GNP/EPON862 shown in Figure 55. The axial CLTEs of hybrid composites increase when increasing GNP volume fraction for all systems which the level of GNP dispersion influents the axial CLTEs. However, the axial CLTE of single-layer GNP system increases at the lower GNP volume fraction and then

the axial CLTE decrease beyond 9 vol% of GNP. The reason of this curve is not only about the changing of CLTE but also the changing of elastic properties in the matrix region. At the low GNP volume fraction, the axial CLTE increases because the stiffness in the matrix region increases and the axial CLTE of carbon fiber is very low. The CLTE of matrix slightly decreases which hardly affects to the overall axial CLTE of the hybrid composites. At the high GNP volume fraction, the CLTE of matrix dramatically decreases and consequentially overcomes the increasing CLTE due to the stiffness so the axial CLTE starts to decrease after this point.

Figure 57 The plot of coefficient of transverse thermal expansion as the function of GNP volume fraction.

Figure 57 shows the transverse CLTEs of CF/GNP/EPON862 hybrid composites of all four different GNP systems. All transverse CLTEs linearly decrease when increasing the GNP volume fraction. The transverse CLTE of composite without GNP is already close to the CLTE of neat epoxy which is higher than the axial CLTE. Therefore, the effect of increasing stiffness does not appear on transverse CLTE. The plot also shows that the transverse CLTEs are depended on the different level of GNP dispersion which the perfect dispersion of GNP gives the most reduction of transverse CLTE of GNP/CF/EPON862

hybrid composites. Moreover, the changing of transverse CLTE is larger an order of magnitude of the change of CLTE in axial direction.

6.4 Conclusions

For the GNP/EPON862 composites, GNP decreases the CLTE for all four different level of GNP dispersion. The perfectly dispersed GNP system has the most CLTE's reduction. The equation for randomizing CLTE by Craft & Christensen and elastic properties by Christensen & Walls can be used to predict the CLTE of GNP/CE system. Even the predicted CLTE of GNP/EPON862 deviates from the experimental value, the trend of CLTE reduction is in good agreement with experiment. For the GNP/CF/EPON862 hybrid composites, both axial and transverse CLTEs are depended on both GNP volume fraction and dispersion. The perfect dispersion of GNP has the most change in both CLTEs. The GNP inclusion in the hybrid composites strongly affects to the transverse CLTE. Finally, this study could be improve including GNP aspect ratio.

CHAPTER 7 IMPROVEMENT OF MICROMECHANICS CALCULATION INCLUDING GNP ASPECT RATIO

7.1 Introduction

The improving of thermal conductivity in composites materials is extremely important as well as the enhancing mechanical properties. Graphene Nanoplatelet (GNP) in polymer composites has been widely investigated to develop the highly thermally conductive composites shown as Table 18. The characteristics of graphitic-based fillers; volume fraction, level of dispersion, orientation, and aspect ratio of fillers play roles to the effective thermal conductivity of composites. The experiments [29] have reported that the larger aspect ratio of GNP causes the relatively higher thermal conductivity in the specimen.

From Chapter 4 to Chapter 6, the GNP aspect ratio was all (Semi infinity) constant during the micromechanics calculation due to the original workflow from Hadden et al. [36]. This workflow the thermal conductivities of MD models which the GNP aspect ratios were infinity due to the periodic boundary condition were randomized by arithmetic average before putting into MAC/GMC. The resultant properties [36] of this method were shown in good agreement with the experiment for the elastic properties.

The micromechanics calculation of epoxy composites regarding aspect ratio of single wall carbon nanotube (CNT) has been studied by M. Radue [113]. There is the different perspective between 1D-infinity CNT and 2D-infinity GNP. In this chapter, we improve the workflow of micromechanics calculation for the thermal conductivity by taking into account the GNP aspect ratio.

Table 18 The characteristics of graphitic-based filler in graphene/polymer composites studied thermal conductivity from literature.

Year	Author	Matrix	Filler Characteristics						Method	Ref
			Filler	Lateral length (nm)	Thickness (nm)	Aspect ratio	Number layers	Amount		
2006	M.T. Hung et al.	EPON862/DETDA	GNP	3000	25	120	70b	1 vol%	SEM	[15]
2007	A. Yu et al.	EPON862/DETDA	GNP	350	1.7	200	4a	1.3 - 25 vol%	AFM/TEM	[29]
			GNP	1700	60	30	169b	2.1-5.4 vol%		
			GNP	1100	25	50	70b	5.4 vol%		
2007	B. Debelak et al.	EPON862/DETDA	GNP	Unk.	Unk.	Unk.	Unk.	20 wt%	-	[11]
2008	S. Ganguli et al.	EPON862/DETDA	Exfoliated Graphite	3900	2-100	39-1950	5-282b	2-20 wt%	Data sheet	[14]
2009	S. Wang, et la.	EPON862/DETDA	GO	2000*	1	2000*	1a	1-5 wt%	AFM	[112]
2011	C.C.Teng et al.	DGEBA/DDS	GNP	Unk.	2.3	Unk.	6b	0.24 - 3.85 wt%	AFM	[25]
2011	F. Yavari et al.	1-octadecanol	graphene	Unk.	Unk.	Unk.	3-4a	4 wt%	HRTEM	[114]
2011	S. Yang et al.	DGEBA	MGNP	4520	10	452	28b	1 wt%	SEM/TEM	[28]
2012	K.M.F. Shahil et al.	EPON862/DETDA	MLG	50-500	0.71b	70-704	2a	1.5-10 vol%	AFM/SEM	[22]
2012	S. Chatterjee et al.	EPON828/Aromatic di-amine	Expanded GNP	Unk.	Unk.	Unk.	Unk.	0.5-2 wt%	-	[10]
2013	C. Min et al.	DGEBA/Anhydride	GNP	Unk.	20-50	Unk.	56-141b	0.54-2.71 vol%	SEM	[20]
2013	S. Chandrasekaran et al.	DGEBA/Anhydride	GNP	20000-50000	12-15	1333-4167	34-42b	1-2 wt%	Data sheet	[9]
2015	J. W. Zha et al.	DGEBA	GNP	1000-20000	5-15	67-4000	14-42b	2 vol%	Data sheet	[30]
2015	L. Diaz-Chacon et al.	DGEBA/Anhydride	GNP-m	10000	45	200	126b	0.26-2.67 vol%	SEM	[19]
2015	M. Shtein et al.	DGEBA/Polyester Triamine	GNP-M5	10000	5-20	725	14-56b	11.7-18.6 vol%	SEM/TEM/AFM	[23]
			GNP-M15	19000	9-20	1255	25-56b	8.6-20.8 vol%		
			GNP-M25	34000	>100	<340	>282b	15.1-18.6 vol%		
			GNP-C2	2000	5-20	175	14-56b	11.8-17.2 vol%		
			GNP-H15	20000	15-100	568	42-282b	8.6-24.2 vol%		
2015	Y. Wang et al.	CE/MHHPA	GNP	10000	4	2500	10a	0.5-8 wt%	SEM/TEM/AFM	[27]
2016	C. Kostagiannakopoulou et al.	DGEBA	GNP	5000	10-12	417-500	20-25	1-15 wt%	Data sheet	[17]
		CE/ACA	GNP	1000	1.07-1.42b	704-939b	3-4	4 wt%	Data sheet	Present

a - value from characterization

b - calculated value based on 0.355 nm/layer

* - estimated value from image

7.2 Micromechanics

Figure 58 The dimensions of GNP and GNP/CE simulation box in RUC.

From Figure 58, the aspect ratio of GNP was defined as the proportion between the lateral length and the thickness of GNP. The total GNP aspect ratio of GNP/CE composites can be determined by

$$a_{GNP} = \frac{L}{t_{GNP}} \quad (32)$$

where L is lateral length of GNP and t_{GNP} is the GNP thickness. In MAC/GMC, the aspect ratio of fiber subcell (a_{cell}) was defined as the ratio between box lengths as show following equation

$$a_{cell} = \frac{t_{box}}{L} \quad (33)$$

where t_{box} and L are the box length along the out-of-plane and the in-plane direction of GNP, respectively. The equation (32) and (33) were combined and derived to obtain the relationship between a_{cell} and a_{GNP} shown as equation (34). The aspect ratio of subcell was determined after the GNP aspect ratio was specified.

$$a_{cell} = \frac{t_{box}}{a_{GNP} \times t_{GNP}} \quad (34)$$

From Figure 58, the doubly $2 \times 2 \times 2$ RUC was used to determine the thermal conductivity of GNP/CE composites with different amount of GNP. The in-plane thermal conductivity of GNP/CE was assigned both direction 2 and 3 of a GNP/CE subcell shown in Figure 58. The out-of-plane thermal conductivity was applied along direction 1. The thermal conductivity of neat CE was put in the other seven subcells. The total aspect ratios of the GNP (a_{GNP}) were chosen to be 1, 10, 50, 100, 200, 1000, and 10000 which the subcell's aspect ratios (a_{cell}) were calculated by using equation (34). The dimensions of GNP (t_{GNP}) and MD simulation box (t_{box}) are shown in Table 19. The thickness of GNP from MD was the result from OPLS-AA force field.

Table 19 The GNP thickness and simulation box length of each system.

MD simulation systems	t_{GNP} (Å)	t_{box} (Å)
1GNP/CE	3.55	41.97
2GNP/CE	7.10	41.26
3GNP/CE	14.20	41.36
4GNP/CE	28.40	40.68

The total GNP mass fractions were increased from 0 to 10 wt% with 1 wt% increments. The volume fraction of GNP/CE (fiber) subcell was calculated using equation (22). After the material properties were assigned to MAC/GMC, the thermal conductivities of GNP/CE were determined for all three axes. The arithmetic average of these three thermal conductivities was obtained to predict the thermal conductivity with all possible rotation

of GNP. The GNP aspect ratio study was applied to all 1, 2, 3, and 4-layer GNP/CE systems.

Table 20 The characteristics of graphene fillers in experimental specimens [22, 29, 112].

Matrix	Filler	Filler Characteristic					Amount	Ref
		Lateral length (nm)	Thickness (nm)	Aspect ratio	Number layers	Method		
EPON862 /DETDA	GNP	350	1.7	200	4	AFM, TEM	1.3-25 vol%	[29]
EPON862 /DETDA	GO	2000*	1	2000*	1	AFM	1-5 wt%	[112]
EPON862 /DETDA	MLG	50-500	0.71 ^a	70-704	2	AFM, SEM	1.5-10 vol%	[22]

*estimated from AFM image

^acalculated based on 0.355 nm/layer of GNP thickness

7.3 Results

The normalized thermal conductivities of 1-layer GNP/CE and 4-layer GNP/CE models with GNP aspect ratio of 1, 10, 50, 100, 200, 1000, and 10000 are shown in Figure 59 and Figure 60, respectively. The predicted thermal conductivities increase as nonlinear relationship with GNP mass fraction. Furthermore, the effective thermal conductivities are higher with the larger aspect ratio of GNP for both different level GNP dispersion. The thermal conductivities of 1-layer GNP/CE models are relatively higher than the thermal conductivities of 4-layer GNP/CE models at the same GNP aspect ratio. This means that the thermal conductivities are the higher with the better dispersion of GNP with same aspect ratio of GNP.

Figure 59 The predicted normalized thermal conductivity of single-layered GNP/CE model with different GNP aspect ratios as the function of GNP mass fraction.

Figure 60 The predicted normalized thermal conductivity of 4-layered GNP/CE model with different GNP aspect ratios as the function of GNP mass fraction.

Figure 61 shows the predicted normalized thermal conductivity of 2-layer GNP/CE model by using the multiscale modeling compared with the experimental normalized thermal conductivity from Shahil et al. [22]. The predicted thermal conductivities increase nonlinearly with the GNP volume fraction. The predicted thermal conductivity in agreement with the experimental thermal conductivity up to 5 vol% graphene. After 5 vol% of graphene, the thermal conductivities from the experiment are lower than the predicted values which possibly have the GNP agglomeration in the experimental specimens.

Figure 61 Plot of normalized thermal conductivities of 2-layer (Aspect ratio 704) GNP/CE models as the function of GNP volume fraction and the experimental values from Shahil et al. [22].

Figure 62 shows the normalized thermal conductivity for 4-layer GNP/CE model as the function of GNP volume fraction predicted by using multiscale modeling method. In this plot, the predicted values were determined by using 4-layer GNP system with 200 GNP aspect ratio compared with the experimental values from Yu et al. [29]. The predicted

thermal conductivities increase nonlinearly with GNP volume fraction. At 10 vol% GNP and below, the experimental normalized thermal conductivities are higher than the predicted results, however, they have similar trend. For the systems with 20 and 25 vol% GNP, the normalized thermal conductivities for the experiment are lower than the predicted values which the GNP agglomeration possibly occurs in the experiment.

Figure 62 Plot of normalized thermal conductivities of 4-layer (Aspect ratio 200) GNP/CE models as the function of GNP volume fraction and the experimental values from Yu et al. [29].

Another prediction of thermal conductivity is shown in Figure 63. The predicted normalized thermal conductivities of GNP/CE models were calculated by specifying single-layer GNP with 2000 GNP aspect ratio compared with experimental results taken from Wang et al. [112]. The predicted thermal conductivity increases linearly when having the higher GNP volume fraction. For 0.5 vol% GNP, the predicted value is lower than the experiment. At 2.5 vol% GNP, the thermal conductivity from multiscale modeling is in good agreement with the experimental thermal conductivity.

Figure 63 Plot of normalized thermal conductivities of 1-layer (Aspect ratio 2000) GNP/CE models as the function of GNP volume fraction and the experimental values from Wang et al. [112].

7.4 Conclusions

Micromechanical modeling can successfully predict the effective thermal conductivity of GNP/CE system by using MAC/GMC. GNP aspect ratio is one of important GNP characteristics to improve the thermal conductivity. The thermal conductivity does not only increase with the GNP volume fraction and better GNP dispersion but it also increases with the GNP aspect ratio. However, this study omitted the thermal pathway which the nanoparticles are connected and able to transfer the heat, effectively. This could further investigate the fully feature of GNP characteristics by using mesoscale modeling or finite element method.

CHAPTER 8 RECOMMENDATIONS FOR FUTURE WORK

8.1 Mesoscale Modeling

Mesoscale modeling has capability to study the model at the larger scale combining with information from MD modeling. The thermal conductivity of GNP/CE is potentially investigated more about the orientation. This means how each different orientation GNP in a large model interacts to each other which the pathway or agglomeration can be captured at this level. The mixing of different level of GNP dispersion is another interesting topic to be studied because the experimental specimen always has the mix of different GNP thickness and lateral length.

8.2 The Glass-Transition Temperature on GNP/CE Composites

The glass-transition temperature of GNP/CE composites have not yet been studied which is an important materials property. The mechanical properties usually decrease when using the materials above the glass-transition temperature. The characteristic of GNP that could affect to the glass-transition temperature include the level of dispersion, aspect ratio, and orientation.

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Appendix A Computational Resources

A.1 HPC specification (Michigan Tech)

	Athena	Superior
No. of compute nodes	27	72
No. of CPU cores per node	12	16
CPU type	Intel Xeon X5650	Intel Sandy Bridge E5-2670
CPU speed	2.67 GHz	2.60 GHz
RAM per node	24 GB	64 GB
Storage	13 TB	48 TB

A.2 Computing Time

Most of the MD simulations were run on Superior HPC, few of monomers simulation were run on Athena HPC.

A.2.1 Neat Cycloaliphatic Epoxy

Number of atoms per model: 7164 (Cube) and 10746 (Prism)

System	Simulation Description	Simulation Time (ns)	No. of Proc.	CPU time (hrs)
	Monomers*	3	16-32	3
Cube - mechanical properties	Densification	26.5	16	591
	Crosslink - 100 cycles	2	64	5567
	Relaxation	10.5	16	652
	Tensile deformation	30	16	4414
Prism - thermal properties	Densification	26.5	16	1435
	Crosslink - reaching to 90%	15.5	16	3185
	Relaxation	73.5	16	2992
	NEMD for thermal conductivity	70.35	16	4791
Cube - thermal properties	Crosslink - reaching to 90%	11.42	16	1069
	Relaxation	73.5	16	1780
	Heating-up simulation for Tg and CLTE	192.5	16	8712
	EMD for thermal conductivity	350.35	16	13179

*Using Athena and Superior HPC

A.2.2 Graphene Nanoplatelet/Cycloaliphatic Epoxy

Number of atoms per model: 5886-5949

Simulation Description	Simulation Time (ns)	No. of Proc.	CPU time (hrs)
Graphene	0.8	16	4
Densification	106	16	5346
Crosslink - reaching to 80%	55.7	16	4691
Relaxation	42	16	1192
EMD for thermal conductivity	200.2	16	7320

A.2.3 Functionalized Graphene Nanoplatelet/Cycloaliphatic Epoxy

Number of atoms per model: 5989-6029

Simulation Description	Simulation Time (ns)	No. of Proc.	CPU time (hrs)
Functionalized graphene	3.2	16	19
Densification	53	16	1991
Crosslink - reaching to 80%	31.12	16	14278
Relaxation	21	16	1430
EMD for thermal conductivity	100.1	16	3684

A.2.4 CLTE of GNP/EPON862

Number of atoms per model: 24950-37550

Simulation Description	Simulation Time (ns)	No. of Proc.	CPU time (hrs)
Relaxation	8.4	16	816
Heating up and cooling down	42	16	3494

Appendix B Copyright documentation

B.1 Copyright of Figure 1, Figure 2, and Figure 3

Michigan Tech

Sorayot Chinkanjanarot <schinkan@mtu.edu>

Request for using pictures in dissertation
4 messages

Sorayot Chinkanjanarot <schinkan@mtu.edu>
To: dbryant@ctcglobal.com

Thu, Oct 19, 2017 at 3:32 PM

Hello Dave,

My name is Sorayot Chinkanjanarot, a graduate student in HVT center from Michigan Tech.
Now, I am writing my dissertation to finish my degree.

Can I use these pictures of yours in my dissertation, please?
(I downloaded them from wikipedia and Facebook page.)
<https://goo.gl/dXSSy6>
https://en.wikipedia.org/wiki/ACCC_conductor

Thank you.
Best regards,
Sorayot (Choi) Chinkanjanarot

PhD student in Mechanical Engineering-Engineering Mechanics
Department of Mechanical Engineering-Engineering Mechanics
Michigan Technological University

3 attachments

20156032_1336862239760320_4218867494602872096_n.jpg
44K

ACSR_and_ACCC.JPG
3872K

Sag_Comparison_Test_Data.jpg
87K

Dave Bryant <dbryant@ctcglobal.com>

Thu, Oct 19, 2017 at 4:08 PM

To: Sorayot Chinkanjanarot <schinkan@mtu.edu>

No problem. Good luck and best regards.

Dave Bryant
Director Technology
CTC Global
[2026 McGaw Avenue](https://www.ctcglobal.com)
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B.2 Copyright of Figure 6

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Title: Graphene–Multilayer Graphene Nanocomposites as Highly Efficient Thermal Interface Materials

Author: Khan M. F. Shahil, Alexander A. Balandin

Publication: Nano Letters

Publisher: American Chemical Society

Date: Feb 1, 2012

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Appendix C Codes and Scripts

C.1 Densification script

This script is to compress the simulation box to general mass density of epoxy as mentioned above.

```
#-----initialization-----
```

```
units          real
dimension      3
boundary       p p p
atom_style     molecular
```

```
#-----force-field-----
```

```
bond_style     harmonic
angle_style    harmonic
dihedral_style opls
```

```
pair_style     lj/cut 10.0
read_data      c7x14e1_nov11.mol
```

```
replicate      3 2 2
```

```
#-----dimension-----
```

```
variable       denneat equal 1.2          #density of neat CE [g/cc]
group          ce type 1:33                #group of neat CE
variable       mce equal mass(ce)          #mass of CE
variable       cc2cA equal 10^24           #convert cubic centimeter to cubic angstrom
#length of CE in x, y, and z direction
variable       xyz equal ((v_mce*1.66e-24/v_denneat)*v_cc2cA)^(1/3)
print          "x,y,z are equal $(v_xyz)"
```

```
#-----settings-----
```

```
timestep       1
variable       Time equal step*dt/1000 #time in picoseconds
```

```
fix            1 all nvt temp 300 300 100000
fix            2 all deform 1 x final $(v_xyz*2/2) $(v_xyz*2/2) y final $(v_xyz*2/2) \
              $(v_xyz*2/2) z final $(v_xyz*2/2) $(v_xyz*2/2) units box
```

thermo_style custom step v_Time temp press etotal ke pe ebond eangle edihed evdwl \ density

#NOTE: time (and velocity) do not exist in a minimization

dump 1 all atom 10 den_c7x14e1_2nd_minimization.lammpstrj #every 10 steps

dump_modify 1 scale no sort id

min_style cg

minimize 1.0e-4 1.0e-6 100 1000

undump 1

reset_timestep 0

velocity all create 300 2549801 rot yes mom yes

thermos 1000 #every picosecond

log den_c7x14e1_2nd_dynamics.log.lammps

dump 1 all atom 1000 den_c7x14e1_2nd_dump.lammpstrj #every picosecond

dump_modify 1 scale no sort id

run 200000 #200 picoseconds

#Minimize to reducing system's energy#2

minimize 1.0e-4 1.0e-6 100 1000

#Run for squeezing precisely #2

unfix 2

fix 3 all deform 1 x final $\$(-v_{xyz}*1.15/2)$ $\$(v_{xyz}*1.15/2) \setminus$
y final $\$(-v_{xyz}*1.15/2)$ $\$(v_{xyz}*1.15/2) \setminus$
z final $\$(-v_{xyz}*1.15/2)$ $\$(v_{xyz}*1.15/2)$ units box

run 1000000

#Minimize to reducing system's energy#3

minimize 1.0e-4 1.0e-6 100 1000

#Run for squeezing precisely #3

unfix 1

unfix 3

fix 4 all nvt temp 300 300 100000

fix 5 all deform 1 x final $\$(-v_{xyz}*1.05/2)$ $\$(v_{xyz}*1.05/2) \setminus$
y final $\$(-v_{xyz}*1.05/2)$ $\$(v_{xyz}*1.05/2) \setminus$
z final $\$(-v_{xyz}*1.05/2)$ $\$(v_{xyz}*1.05/2)$ units box

run 2000000

#Minimize to reducing system's energy#4

minimize 1.0e-4 1.0e-6 100 1000

#Run for squeezing precisely #4

unfix 4

```

unfix      5
fix        6 all nvt temp 300 273 100000
fix        7 all deform 1 x final $(-v_xyz/2) $(v_xyz/2) y final $(-v_xyz/2) \
          $(v_xyz/2) z final $(-v_xyz/2) $(v_xyz/2) units box
run        2000000

#Minimize to reducing system's energy#5 (final)
minimize   1.0e-4 1.0e-6 100 1000

write_data den_c7x14e1_2nd.data
write_restart den_c7x14e1_2nd.restart

#Check density profile
unfix      7
undump 1

compute    cd1 all chunk/atom bin/1d x lower $(lx/20)
fix        8 all ave/chunk 100 10 1000 cd1 density/mass ave running \
          file den_x.profile

compute    cd2 all chunk/atom bin/1d y lower $(ly/20)
fix        9 all ave/chunk 100 10 1000 cd2 density/mass ave running \
          file den_y.profile

compute    cd3 all chunk/atom bin/1d z lower $(lz/20)
fix        10 all ave/chunk 100 10 1000 cd3 density/mass ave running \
          file den_z.profile

run        100000

```

C.2 Crosslink Scripts Package for pure CE

The crosslink script package includes initial crosslink scripts (LAMMPS), bond-updating scripts (Python), angle and dihedral-updating script (Python), relaxing script(LAMMPS), and control script (Bash).

C.2.1 Initial crosslink script (LAMMPS)

The crosslink script is for creating the initial bond shown as following.

```
#-----initialization-----
```

```
units          real
dimension      3
boundary       p p p
atom_style     molecular
```

```
#-----force-field-----
```

```
bond_style     harmonic
angle_style    harmonic
dihedral_style  opls

pair_style     lj/cut 15.0
read_data      den_c7x14e1_nov11.data
special_bonds  lj/coul 0 1 1 extra 32
```

```
#-----settings-----
```

```
timestep       0.1
variable Time equal step*dt/1000 #time in picoseconds
thermo_style    custom step v_Time temp press etotal ke pe ebond eangle edihed evdwl \
                density
```

```
delete_bonds    all bond 33 remove
delete_bonds    all angle 44 remove
delete_bonds    all dihedral 61 remove
```

```
fix             2 all nvt temp 300 300 10
```

```
#-----run-----
```

```
dump            1 all atom 10 e1r0_c7x14e1_minimization.lammpstrj #every 10 steps
```

```

dump_modify 1 scale no sort id
min_style    cg
minimize     1.0e-4 1.0e-6 100 1000
undump       1
reset_timestep 0

velocity      all create 300 4928459 rot yes mom yes
thermo        1000                      #every picosecond
log           log.e1r0_c7x14e1.lammps
dump          1 all atom 1000 dump.xl-c7x14e1 #every picosecond
dump_modify   1 append yes scale no sort id

#-----crosslinked-processi[Esterification-1]-----
fix           3 all bond/create 1 23 25 7.0 30 iparam 1 29 jparam 1 28 \
              prob 0.001 85784          #create C-O bond for the ester

#-----crosslinked-processi[OpenRing-1]-----

#fix          4 all bond/create 1 26 8 7.0 32 iparam 1 16 jparam 1 15 \
              prob 0.01 85784          #create C-O bond for carboxylate(ester)

#-----minimization after creating bonds-----
run           2000
minimize      1.0e-4 1.0e-6 100 1000

#-----Write outputs-----
write_restart e1r0_c7x14e1.restart
write_data    e1r0_c7x14e1.data

```

C.2.2 Angle and dihedral-updating script (Python)

This package can be downloaded from:

https://github.com/schinkan/PhD_research/tree/master/BAD_script

C.2.3 Relaxing script(LAMMPS)

The script for relaxing the model during crosslink.

```
#-----initialization-----
```

```
units          real
dimension      3
boundary       p p p
atom_style     molecular
```

```
#-----force-field-----
```

```
bond_style     harmonic
angle_style    harmonic
dihedral_style opls
```

```
pair_style     lj/cut 10.0
read_data      e1r1p_c7x14e1.data
```

```
#-----settings-----
```

```
timestep       0.1
variable        Time equal step*dt/1000 #time in picoseconds
```

```
fix            1 all npt temp 300 300 10000 iso 1 1 1000.00
```

```
thermo_style    custom step v_Time temp press etotal ke pe ebond eangle edihed evdwl density
```

```
velocity        all create 300 4928459 rot yes mom yes
thermo          1000                      #every picosecond
log             e1r1p_c7x14e1.npt.relax.log.lammps
dump            1 all custom 500000 dump.e1r1p_c7x14e1.npt.relax.lammpstrj id type x y z
dump_modify     1 sort id
run             1000000                    #1000 picoseconds = 1 nanosecond

write_data      e1r1p_c7x14e1.npt.relax.data
```

C.3 EMD scripts for pure CE

#-----initialization-----

```
units          real
dimension      3
boundary       p p p
atom_style     molecular
variable       kB equal 1.3806504e-23
variable       kCal2J equal 4186.0/6.02214e23
variable       A2m equal 1.0e-10
variable       fs2s equal 1.0e-15
variable       convert equal ${kCal2J}*${kCal2J}/${fs2s}/${A2m}
variable       temp_ini equal 300      #initial temperature of the system
variable       teq equal 10000
variable       trun equal 10000000     # number of step for running simulation
variable       p equal 10000           # correlation length
variable       s equal 5               # sample interval
variable       d equal $p*$s          # dump interval
variable       V equal vol
```

#-----force-field-----

```
bond_style     harmonic
angle_style    harmonic
dihedral_style opls

pair_style     lj/cut 10.0
read_data      xl_c7x14e1_2nd_80.npt.relax.data
```

#-----settings-----

```
timestep      1
variable      Time equal step*dt/1000 #time in picoseconds
```

#-----2nd-equilibrium-run-----

```
#fix          fixed1 gends momentum 1 linear 0 0 0 angular
fix           1 all nvt temp $(v_temp_ini) $(v_temp_ini) 100000
thermo_style   custom step v_Time temp press etotal ke pe ebond eangle edihed evdwl
thermo        $d

run           $(v_teq)

velocity       all scale $(v_temp_ini) mom yes rot yes
#unfix        1
```

```

# thermal conductivity calculation, switch to NVE if desired
#fix          NVE all nve
reset_timestep 0

compute        myKE all ke/atom
compute        myPE all pe/atom
compute        myStress all stress/atom NULL virial
compute        flux all heat/flux myKE myPE myStress
variable        Jx equal c_flux[1]/vol
variable        Jy equal c_flux[2]/vol
variable        Jz equal c_flux[3]/vol
fix            JJ all ave/correlate $s $p $d &
               c_flux[1] c_flux[2] c_flux[3] type auto file J0Jt.dat ave running
variable        scale equal ${convert}/${kB}/${temp_ini}/${temp_ini}/${V*$s*dt}
variable        k11 equal trap(f_JJ[3])*${scale}
variable        k22 equal trap(f_JJ[4])*${scale}
variable        k33 equal trap(f_JJ[5])*${scale}
thermo_style    custom step temp v_Jx v_Jy v_Jz v_k11 v_k22 v_k33
run            $(v_trun)
variable        k equal (v_k11+v_k22+v_k33)/3.0
variable        ndens equal count(all)/vol
print           "average conductivity: $k[W/mK] @ $(v_temp_ini) K, ${ndens} /A^3"

```