A Molecular Dynamics Study of The Mechanical Properties of PLA-CNT Nanocomposites

Supervised By

Professor Dr. A.K.M. Masud

Dept. Of IPE, BUET

Md. Sohanoor Rahman	**201636020**
Mohammad Rokibul Hasan Parvez	**201636041**
Md. Mahedi Khan Jitu	**201636047**

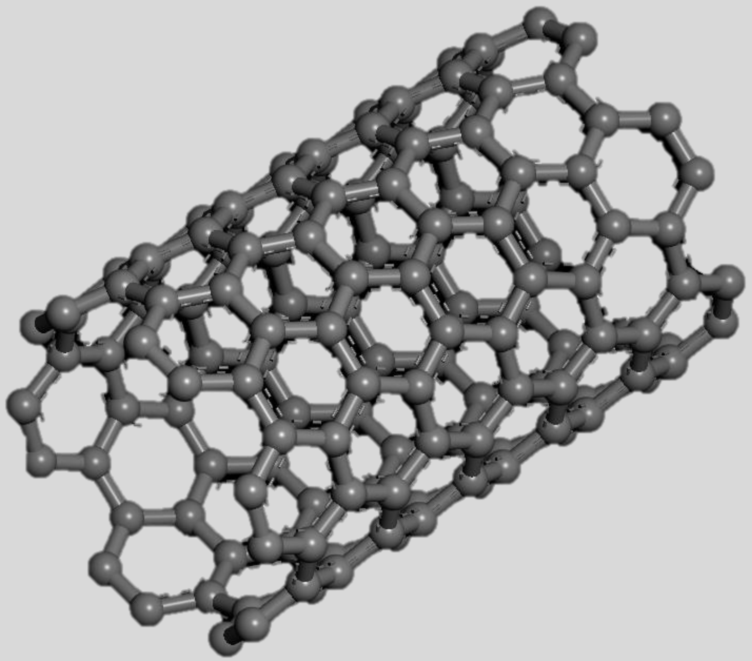
Timeline

1. BACKGROUND
2. LITERATURE REVIEW
3. METHODOLOGY
4. MODEL FORMULATION
5. SIMULATION
6. RESULT AND ANALYSIS
7. CONCLUSION
8. REFERENCE

Introduction

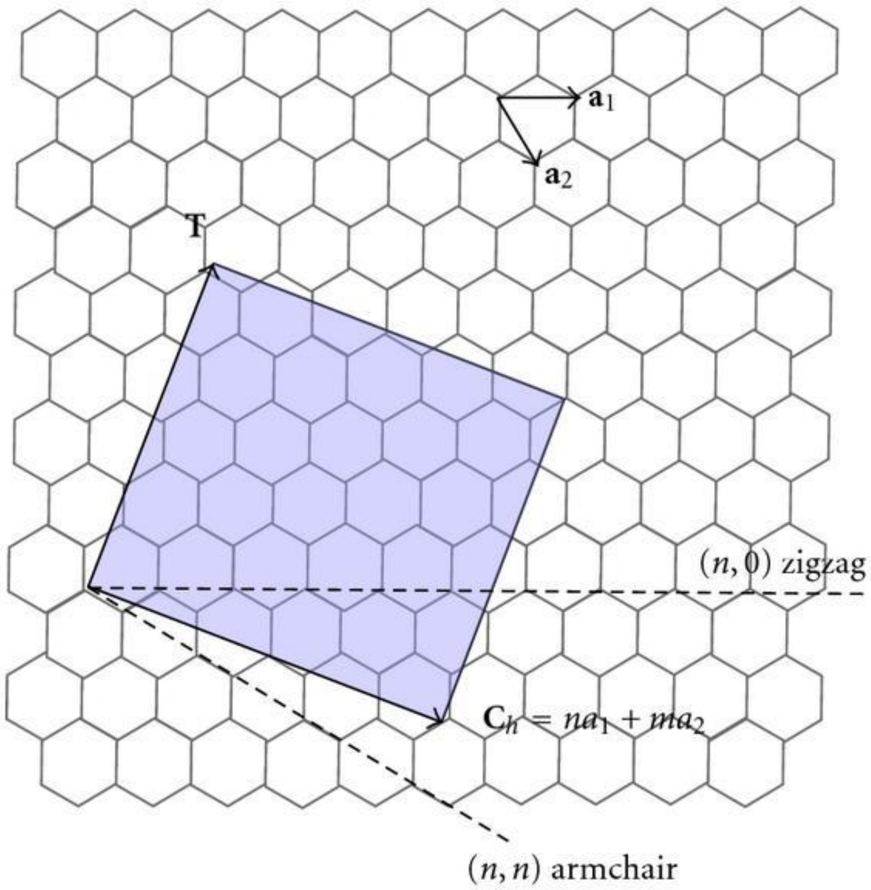
Carbon Nanotube

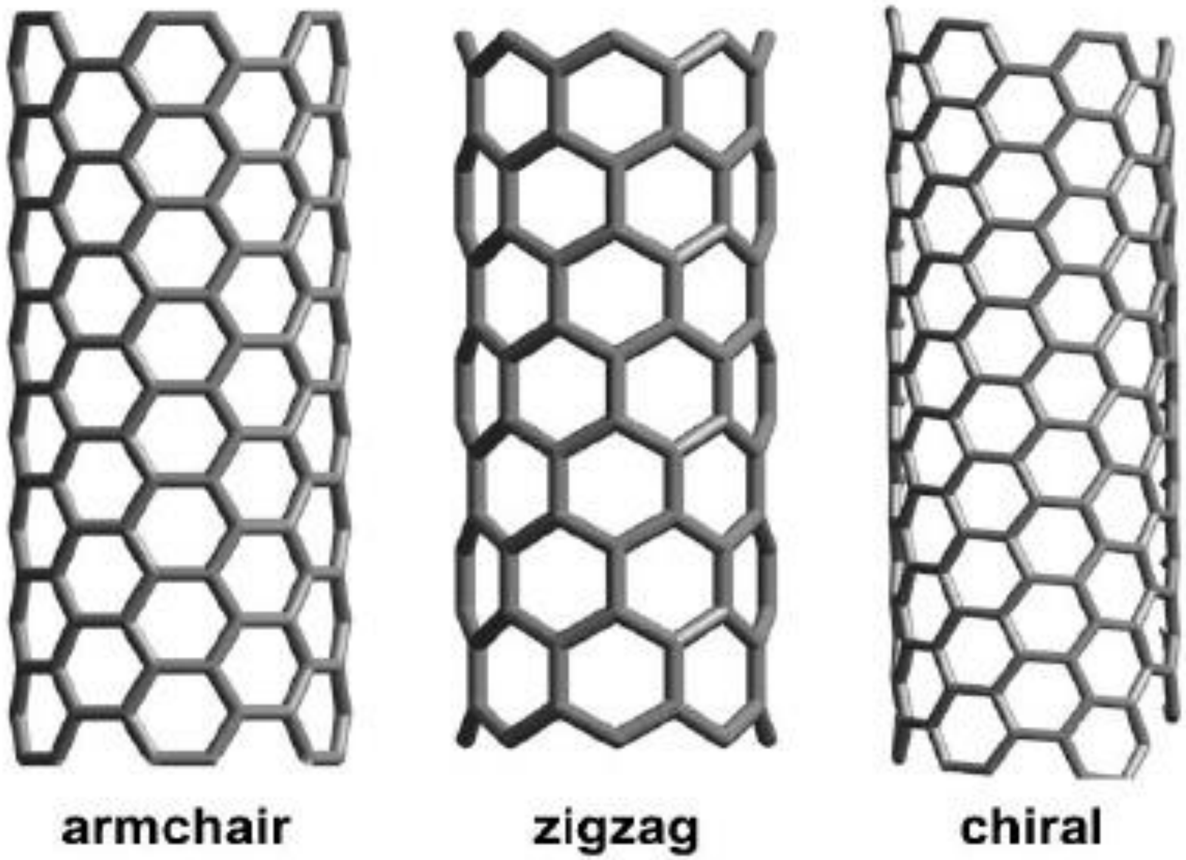
- Discovered by Ijima in 1991
- Two-dimensional hexagonal lattice of carbon atoms, bent and joined in one direction so as to form a hollow cylinder
- Possess higher mechanical, electrical and thermal properties
- Potential reinforcement agents in composite materials for the upcoming ages



Carbon Nanotube

Different Chirality of CNT

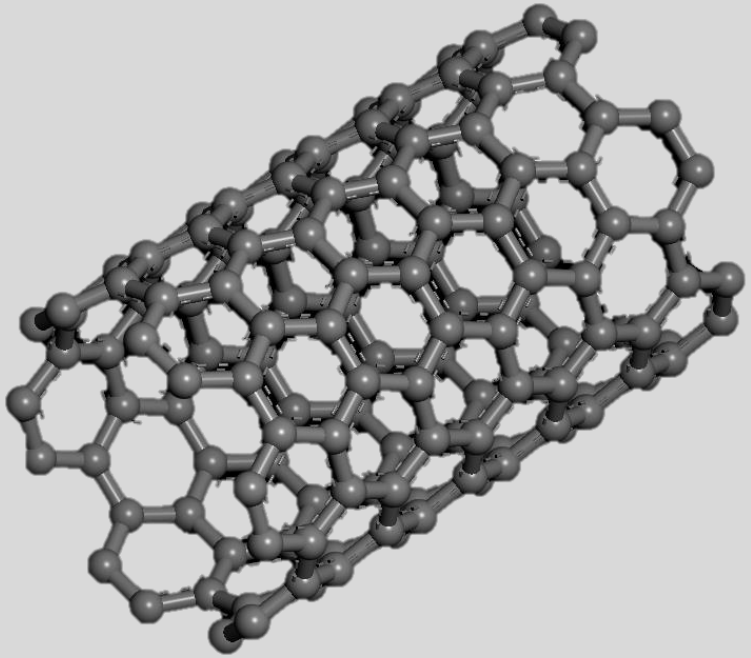




Carbon Nanotube

Mechanical Properties of CNT

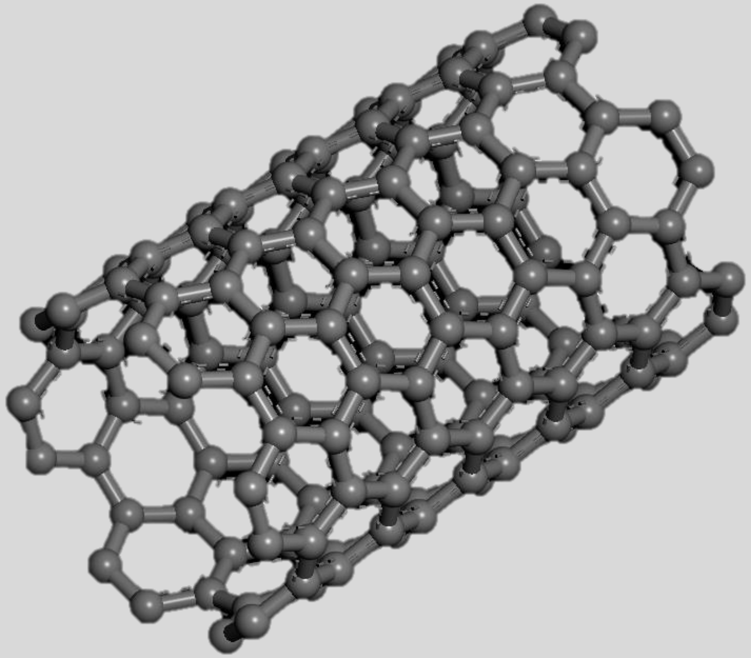
- Brittle in nature
- Tensile strength 11 to 63 GPa
- Young’s modulus 270 to 950 GPa



Carbon Nanotube

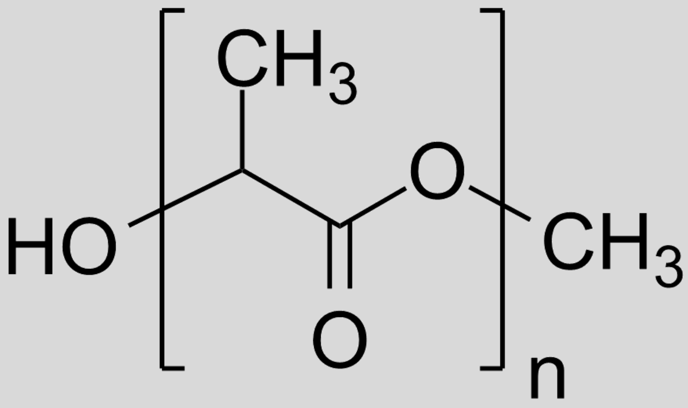
Electrical Properties of CNT

- Exhibit unique conductive properties
- Resistivity is 0.34×10^{-4} to 1.0×10^{-4} ohm.cm
- Depending on the chirality
  - Can be conductive
  - Can be semi conductive



Polylactic Acid (PLA)

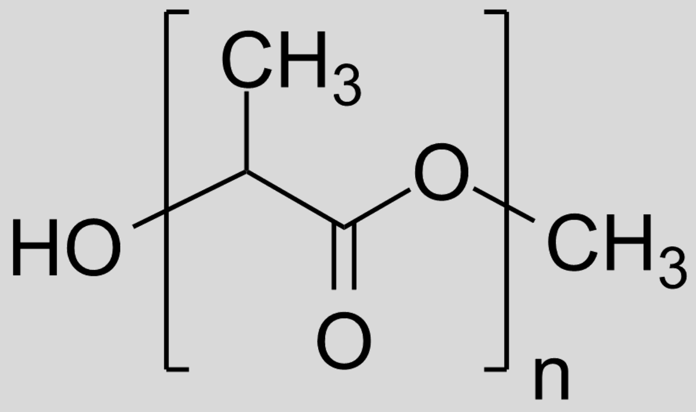
- Discovered in 1932 by Wallace Carothers
- Biodegradable and bioactive polyester
- Manufactured from renewable sources
- Second most produced and consumed bioplastic
- Raw material for current blooming additive manufacturing technology like 3D printing



Polylactic Acid (PLA)

Mechanical Properties of PLA

- Varied to a large extent
  - Soft and elastic plastics (Amorphous)
  - Stiff and high strength materials (Semi-crystalline)
- Young's modulus for PLA can vary 1.1 GPa to 4.1 GPa
- Tensile strength of 50–170 MPa



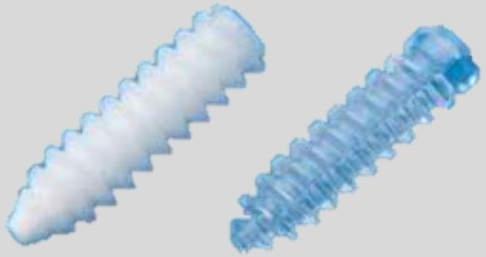
Chemical formula of PLA

Polylactic Acid (PLA)

Potentiality of PLA

- Eco-friendly product with better features for use in the human body (nontoxicity)
- Monomers are produced from non-toxic renewable feedstock
- Production consumes carbon dioxide
- Natural choice for biomedical applications


PLA printing filament


PLA medical screws

Literature Review

Literature Review

Year of Publication	Title	Authors	Findings
1994	Aligned carbon nanotubes arrays formed by cutting a polymer resin-nanotube composite	Ajayan et al	Mixing a small percentage of CNT with polymer significantly **increase the tensile strength** of polymer composite
2007	Molecular dynamics simulation of the elastic Properties of polymer/carbon nanotube composites	Han Y et al	Using MD simulation, estimated the elastic properties of polymer/carbon nanotube composites for **different volume fraction of CNT**.
2012	Investigation of the mechanical properties of polyethylene/carbon nanotube composite by molecular dynamics simulation	Masud AKM et al	Mechanical properties of SWNT reinforced polyethylene (PE) using molecular dynamics (MD) simulation which **satisfactorily reproduces experimental result**

Literature Review

Year of Publication	Title	Authors	Findings
2016	Physical and Mechanical Properties of PLA, and Their Functions in Widespread Applications - A Comprehensive Review	Farah et al	Eco friendly, bio compatibility, bio degradable and consumes CO_2, thus making it **promising material** for future polymer industry
2019	PLA/Graphene/MWCNT Composites with Improved Electrical and Thermal Properties Suitable for FDM 3D Printing Applications	Ivanov et al	The obtained composites are suitable for the production of a multifunctional filament with improved electrical and thermal properties for different fused deposition modelling (FDM) **3D printing applications** and also present a low production cost

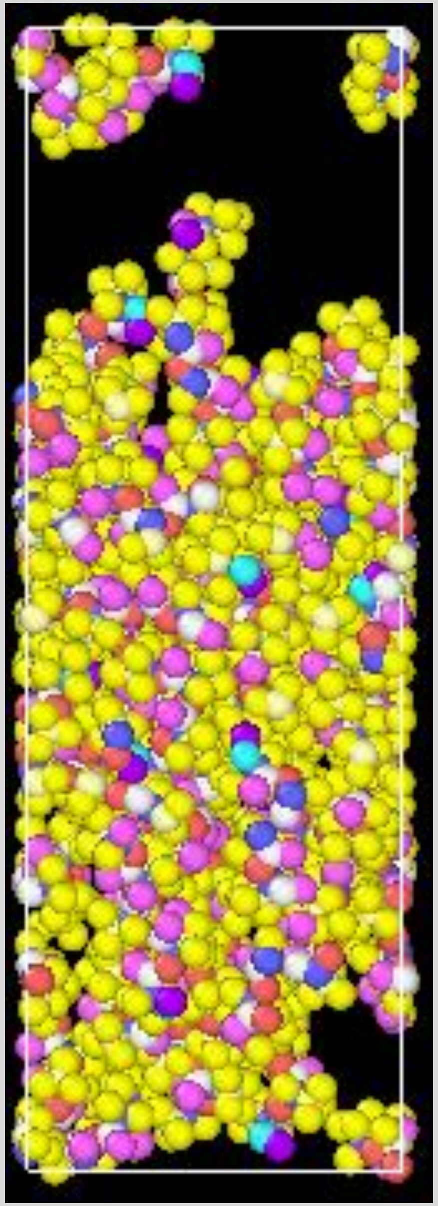
- Alongside above stated other papers provided motivation for non destructively testing mechanical properties of PLA-CNT nanocomposite through molecular dynamics simulation

Methodology

Methodology

MD Simulation

- Computer simulation method for analysing the physical movements of atoms and molecules
- Trajectories of atoms and molecules are determined by numerically solving Newton's equations of motion for a system of interacting particles
- Requires the definition of a potential function
- Flexible enough to run simulation in parallel



Methodology

Process Overview

Generation of Single Polymer Chain and CNT

Packing of Polymer chain around CNT

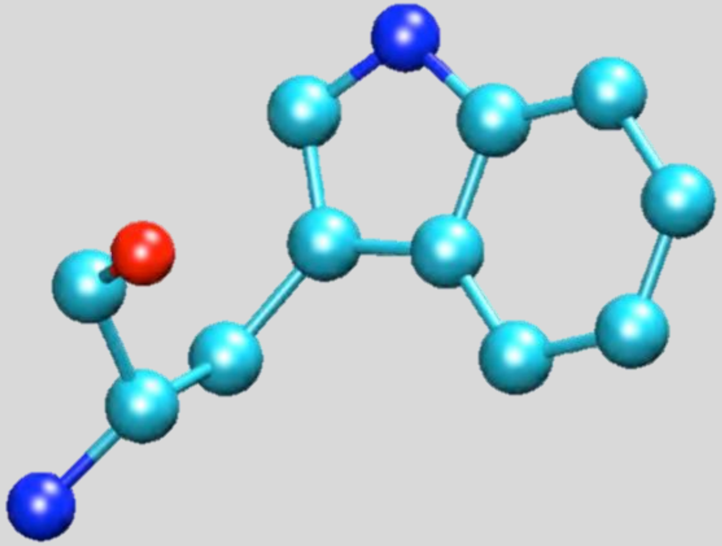
Creating Compatible Data File

Performing MD simulation

Methodology

Forcefield

- Potential energy function
- Collection of equation and associated constants
- Designed to reproduce
  - Molecular geometry
  - Selected properties of tested structures



Methodology

CVFF Forcefield

- **C**onsistent-**V**alence **F**orce**F**ield (CVFF) is a generalized valence forcefield
- Defines atom types for the 20 commonly occurring amino acids, most hydrocarbons, and many other organic molecules
- Atom types CVFF covers hydrogen, carbon, nitrogen, oxygen, sulphur, phosphorus, halogens, ions, argon and silicon
- Parameterized, tested and validated for most of the common organic and inorganic materials
- Ideal for PLA, CNT and PLA-CNT nanocomposite

Methodology

CVFF Forcefield

- $E_{pot} = E_{valence} + E_{nonbond}$
- $E_{valence} = E_{diagonal} + E_{coupling}$
- $E_{diagonal} = E_{bond} + E_{angle} + E_{torsion} + E_{out\text{-}of\text{-}plane}$
- $E_{nonbond} = E_{elec} + E_{vdw}$

$E_{valence}$ is the valence component energy.
$E_{diagonal}$ is the diagonal term energy.
$E_{coupling}$ is the coupling term energy.
E_{bond} is the bond stretching energy.
E_{angle} is the angle energy.
$E_{torsion}$ is the torsion energy.
$E_{out\text{-}of\text{-}plane}$ is the out-of plane deformation energy.
$E_{nonbond}$ is the non-bond energy between atoms in different molecules and atoms separated by three or more bonded atoms.
E_{elec} is the term for Coulombic electrostatic interaction
E_{vdw} is the term for Van der walls energies.

Methodology

CVFF Forcefield

$$E_{bond} = \sum_b D_b[1 - e^{-a}(b - b_0)]^4 \quad E_{angle} = \sum_\theta H_\theta(\theta - \theta_0)^2$$

$$E_{torsion} = \sum_\varphi H\varphi\,[1 - \cos(n\varphi)] \quad E_{out-of-plane} = \sum_\chi H_x X^2$$

$$E_{coupling} = \sum_b \sum_{b'} F_{bb'}(b - b_0)\,(b' - b'_0) + \sum_\theta \sum_{\theta'} F_{\theta\theta'}(\theta - \theta_0)\,(\theta' - \theta'_0) + \sum_b \sum_\theta F_{b\theta}(b - b_0)\,(\theta - \theta_0) + \sum_\varphi F_{\varphi\theta'\theta} \cos(\theta - \theta_0)(\theta' - \theta'_0) + \sum_X \sum_{X'} F_{XX'} XX'$$

$$E_{elect} = \sum \frac{q_i q_j}{\varepsilon r_{ij}}$$

$$E_{vdW} = \sum \varepsilon \left[\left(\frac{r^0}{r}\right)^{12} - 2\left(\frac{r^0}{r}\right)^6 \right]$$

Methodology

Input structure in LAMMPS

Step 1: Initialization

Parameter required for simulation is defined

- Units
- Boundary conditions
- Atom style
- ForceField parameters

Step 2: Atom definition

- Atom co-ordinate generation
- Data file with molecular tropology information
- Use *read_data* command

Methodology

Input structure in LAMMPS

Step 3: Simulation condition

Condition required for simulation is applied

- Equilibrium stage
- NPT conditions
- Final pressure setting
- Final temperature setting

Step 4: Run simulation

- Specify required force and direction using '*fix deform*' command
- Declare variable as required
- Select suitable *erate*
- Run simulation for reasonable amount of timesteps

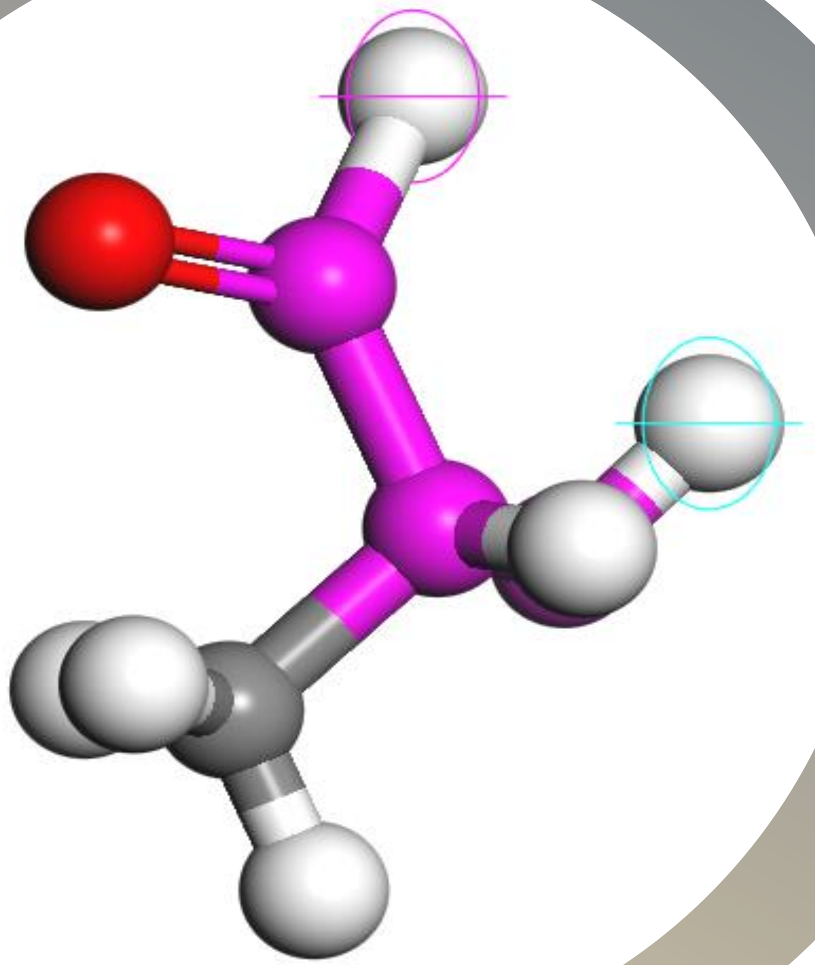
Model Formulation

Model Formulation

Materials Studio

- Software for simulating and modelling materials
- Used in advanced research of various materials, such as polymers, carbon nanotubes, catalysts, metals, ceramics
- Compatible with various forcefields
- Suitable for packing and modelling of nanocomposite

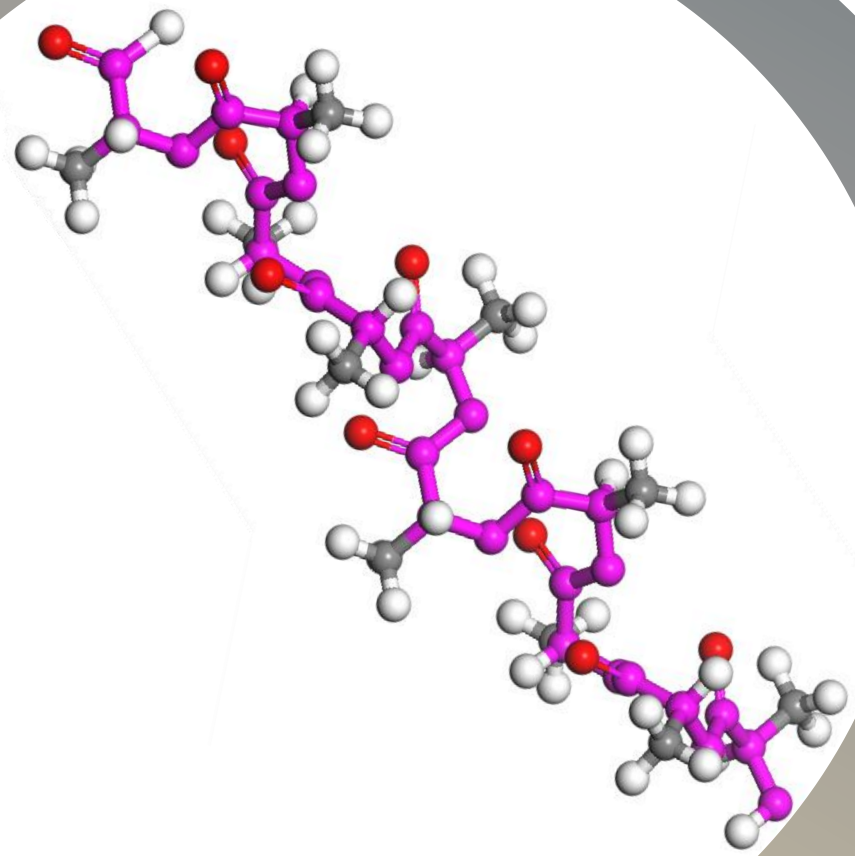
Model Formulation



Material Modeling of Lactic Acid

- Molecular formula $C_3H_6O_3$
- Chiral in nature
- 3 Oxygen atoms and 6 Hydrogen atoms bonded around 3 Carbon atoms

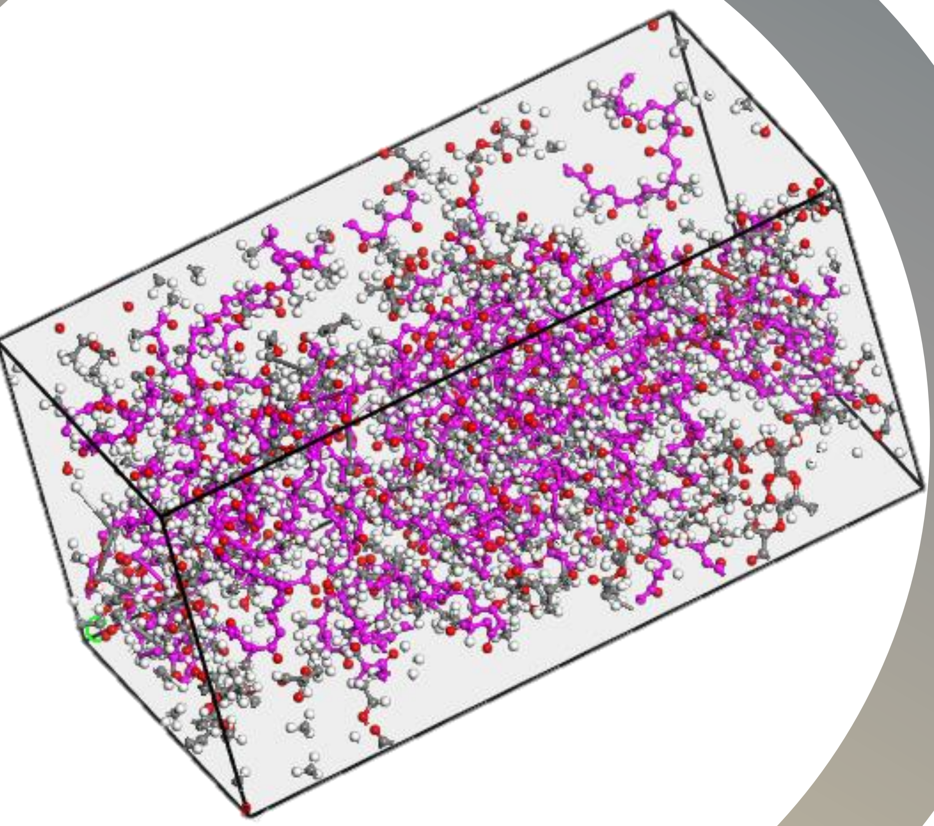
Model Formulation



Material Modeling of PLA

- Molecular formula $(C_3H_4O_2)_n$
- Repeat unit $C_3H_4O_2$
- Polymer formed with 10-15 repeat unit depending on the packing

Model Formulation



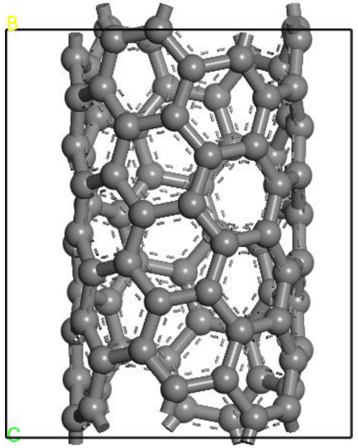
Amorphous packing of PLA

- Amorphous packing of PLA
- Geometry optimized with CVFF forcefield
- Using packing density of 1.23 g/cm^3
- Lattice type 3D triclinic
- Lattice lengths A=30 Å, B=30 Å, C=60 Å

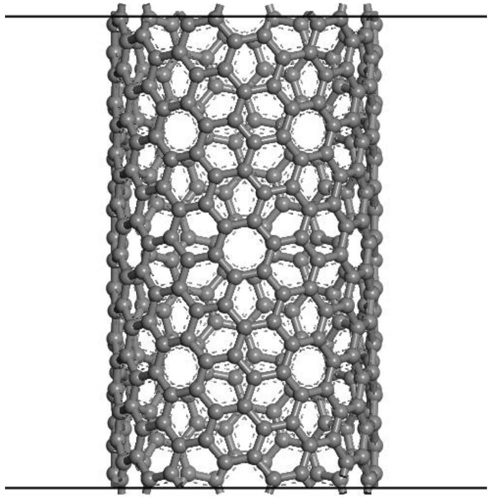
Model Formulation

Material Modeling of CNT

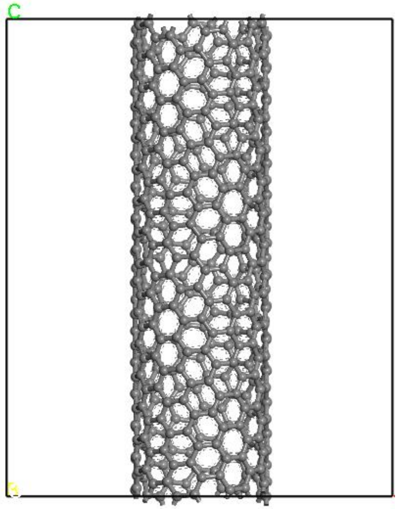
In order to prepare PLA-CNT nanocomposite model, Single walled carbon nanotube (SWNT) of chirality (3,6), (6,9), (6,12) are modelled.



3,6



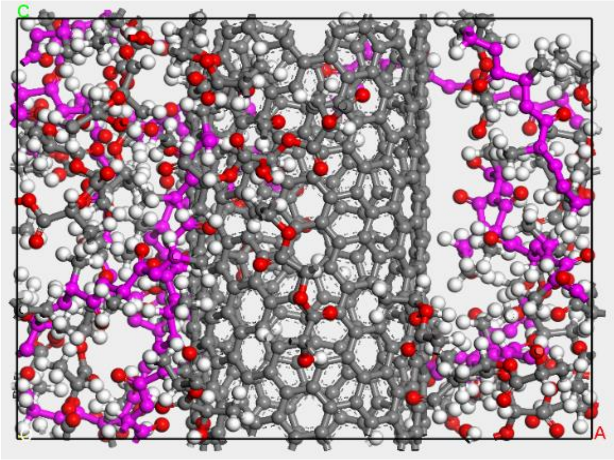
6,9

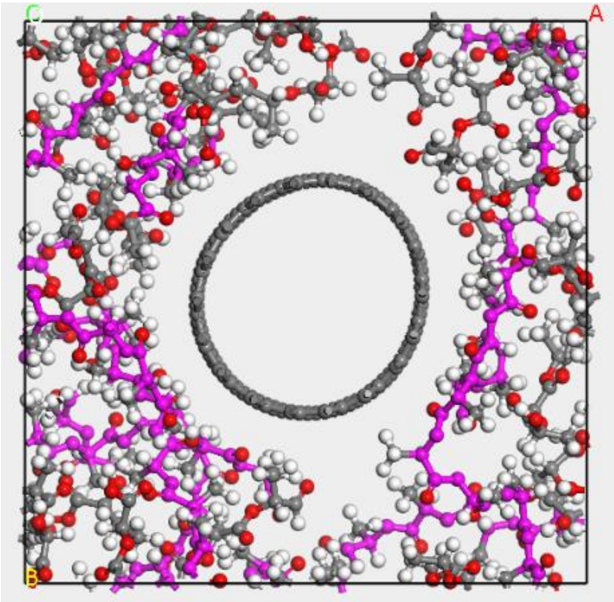


6,12

Chirality	Length (Å)	Diameter (Å)	Lattice Parameter ($Å^3$)
(3,6)	22.54	6.12	31×31×22.54
(6,12)	22.54	12.43	25×25×22.54
(6,9)	37.14	10.24	30×30×37.14

Model Formulation





Amorphous Packing of PLA-CNT Nanocomposite

- Amorphous packing of PLA-CNT nanocomposite
- Geometry optimized with CVFF forcefield
- Packing density of 1.01 g/cm^3
- Lattice type 3D triclinic

Model Formulation

Transforming Model to Simulation Data Cell

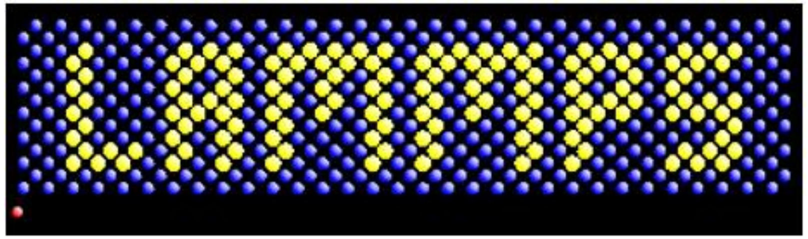
msi2lmp software

Packing	CNT volume fraction	Atoms	Bonds	Angles	Dihedrals	Impropers
PLA	N/A	2116	2093	3680	4554	230
PLA-SWNT (3, 6)	12.76%	1484	1540	2744	3724	308
PLA-SWNT (6, 9)	13.60%	2336	2524	4568	6616	656
PLA-SWNT(6,12)	19.60%	1511	1654	3008	4441	461

Input Dataset Summary

MOLECULAR DYNAMICS SIMULATION

Simulation Details



LAMMPS software package

- **L**arge-scale **A**tomic/**M**olecular **M**assively **P**arallel **S**imulator
- Software package for running MD simulation
- Distributed as an open source code
- Computing efficiency increase using
  - Neighbor lists to keep track of nearby particles
  - Parallel simulation in small 3d sub-domain

Simulation Details

LAMMPS Simulation

Step 1: Initialization

Parameter required for simulation is defined

- *units* real
- *boundary* p p p
- *atom_style* full
- *pair_style* lj/cut 10.5
- *bond_style* harmonic
- *angle_style* harmonic

Step 2: Atom definition

- *Neighbor* 0.4 bin
- Use *read_data* command

Simulation Details

Input structure in LAMMPS

Step 3: Simulation condition

Equilibrium stage performed

- NVT dynamics at 500 K for 10,000 timesteps
- NPT dynamics at 500 K for 50,000 timesteps
- To cool down two more 50,000 timestep relaxation is used

Step 4: Run simulation

- Uniaxial tensile deformation simulated at NPT along z direction
- Declared variable as required
- 0.00001 *erate* assigned
- Simulation ran for 100,000 timesteps

RESULT AND ANALYSIS

Result and Analysis

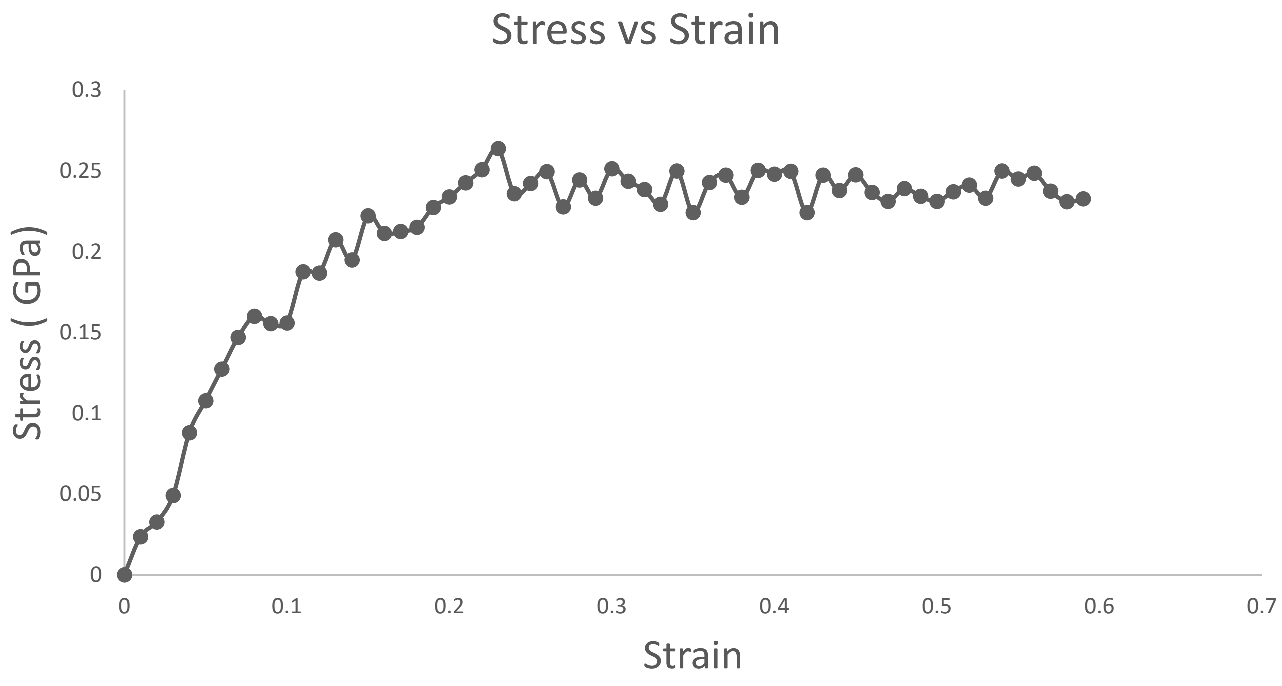
Mechanical Properties of PLA

- Analysis focused on Young’s modulus and tensile strength of PLA polymer by reinforcing carbon nanotube
- MD simulation used to study uniaxial tensile deformation of amorphous PLA and PLA-CNT
- Through simulation process value of Young’s modulus and tensile strength is obtained

- Farah et al (2016) showed that Young’s modulus for PLA can vary 3.7 GPa to 4.1 GPa
- Wang et al (2002) showed for different starch ratio it can vary 1.1 GPa to 1.78 GPa
- Kamthai and Magaraphan (2016) found the value of Young’s modulus to be **2.0043 GPa**

Result and Analysis

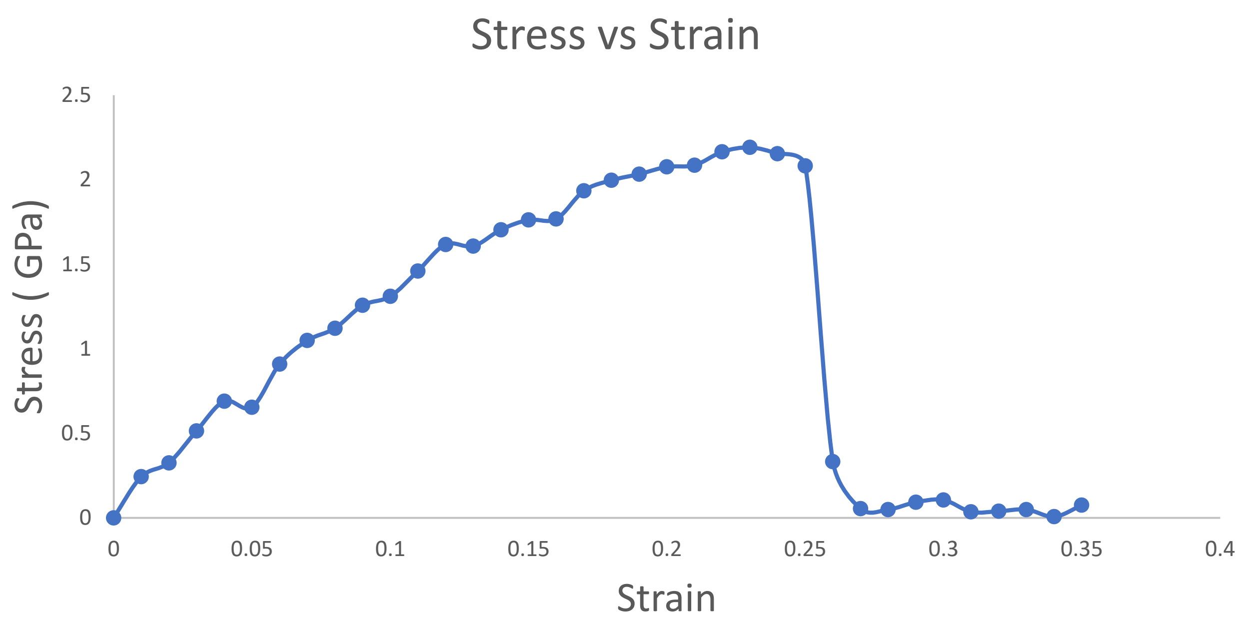
Mechanical Properties of PLA



- Graph generated from strain and pressure tensor obtained from simulation
- Elastic region continues up to around 0.15 GPa
- Plastic region continues from 0.15 GPa onwards
- Result
  - Young's modulus **2.085 GPa**
  - Tensile strength 0.26 GPa

Result and Analysis

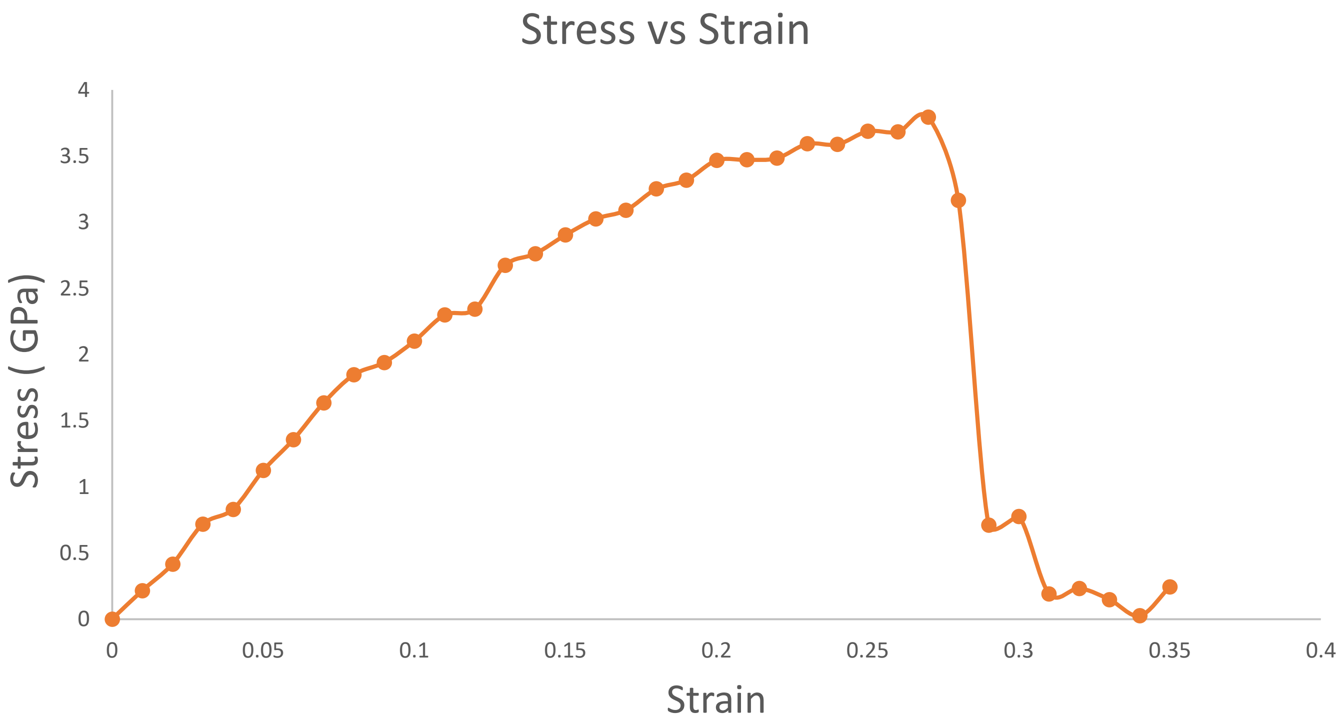
Mechanical Properties of 12.76% PLA-SWNT (3,6)



- Graph generated from strain and pressure tensor obtained from simulation
- Catastrophic failure occurred at 0.25 strain
- Due to CNT reinforcement crack propagation occurred resulting catastrophic failure
- Result
  - Young’s modulus 14.811 GPa
  - Tensile strength 2.19 GPa

Result and Analysis

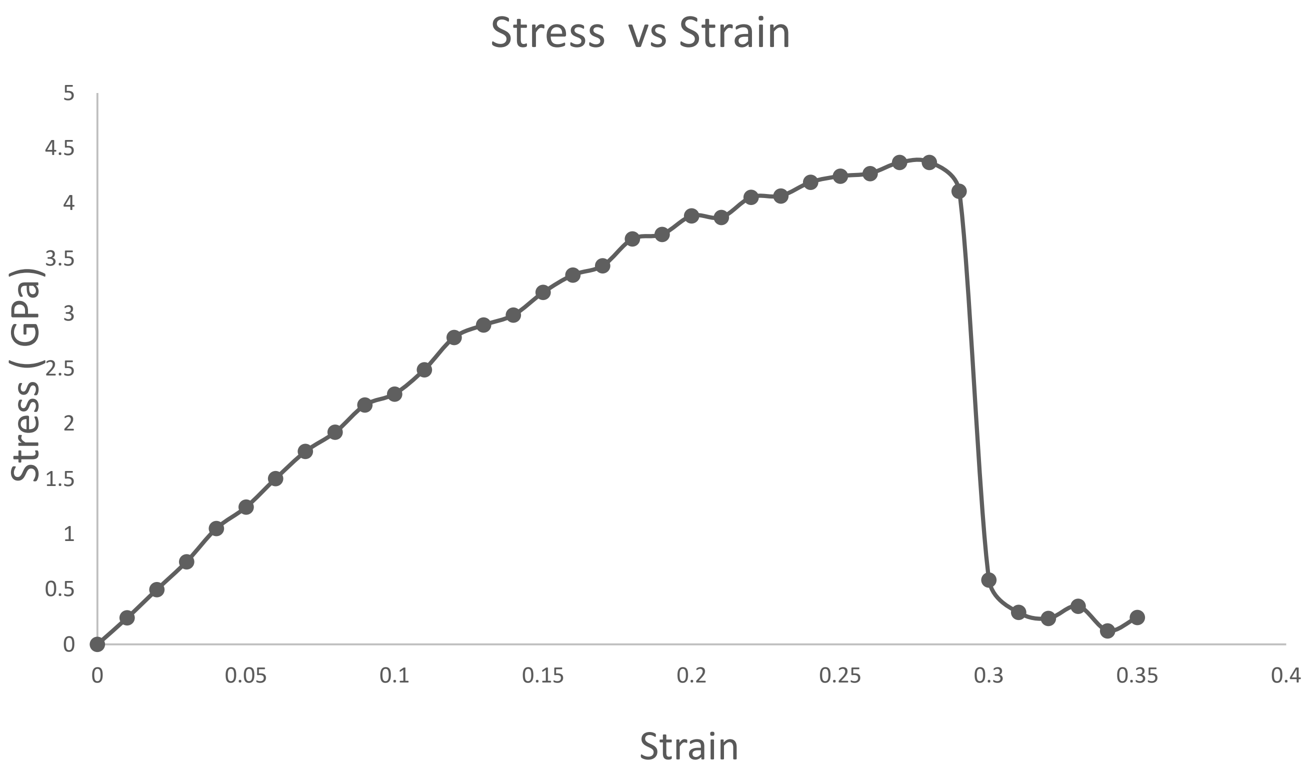
Mechanical Properties of 13.60% PLA-SWNT (6,9)



- Graph generated from strain and pressure tensor obtained from simulation
- Catastrophic failure occurred at 0.28 strain
- Due to CNT reinforcement crack propagation occurred resulting catastrophic failure
- Result
    - Young's modulus 22.795 GPa
    - Tensile strength 3.79 GPa

Result and Analysis

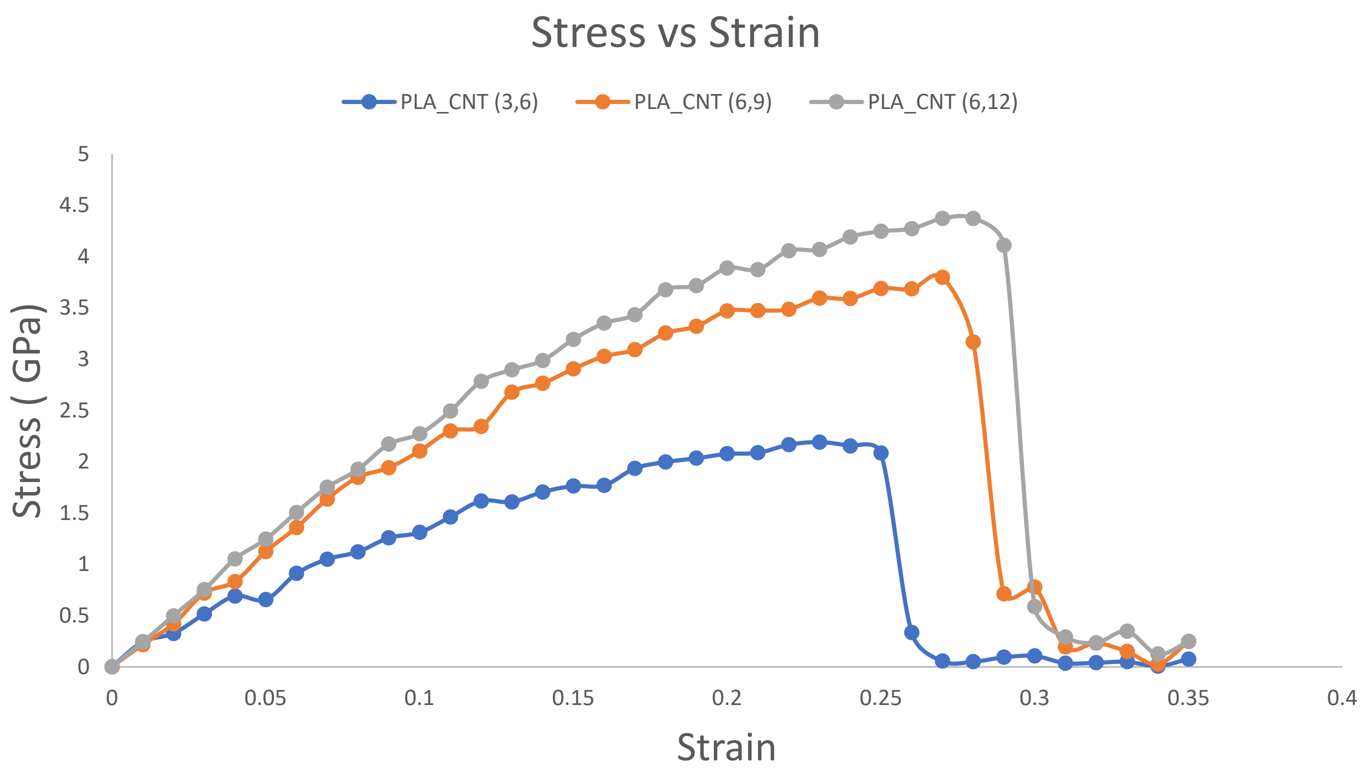
Mechanical Properties of 19.60% PLA-SWNT (6,12)



- Graph generated from strain and pressure tensor obtained from simulation
- Catastrophic failure occurred at 0.29 strain
- Due to CNT reinforcement crack propagation occurred resulting catastrophic failure
- Result
  - Young’s modulus 24.583 GPa
  - Tensile strength 4.37 GPa

Result and Analysis

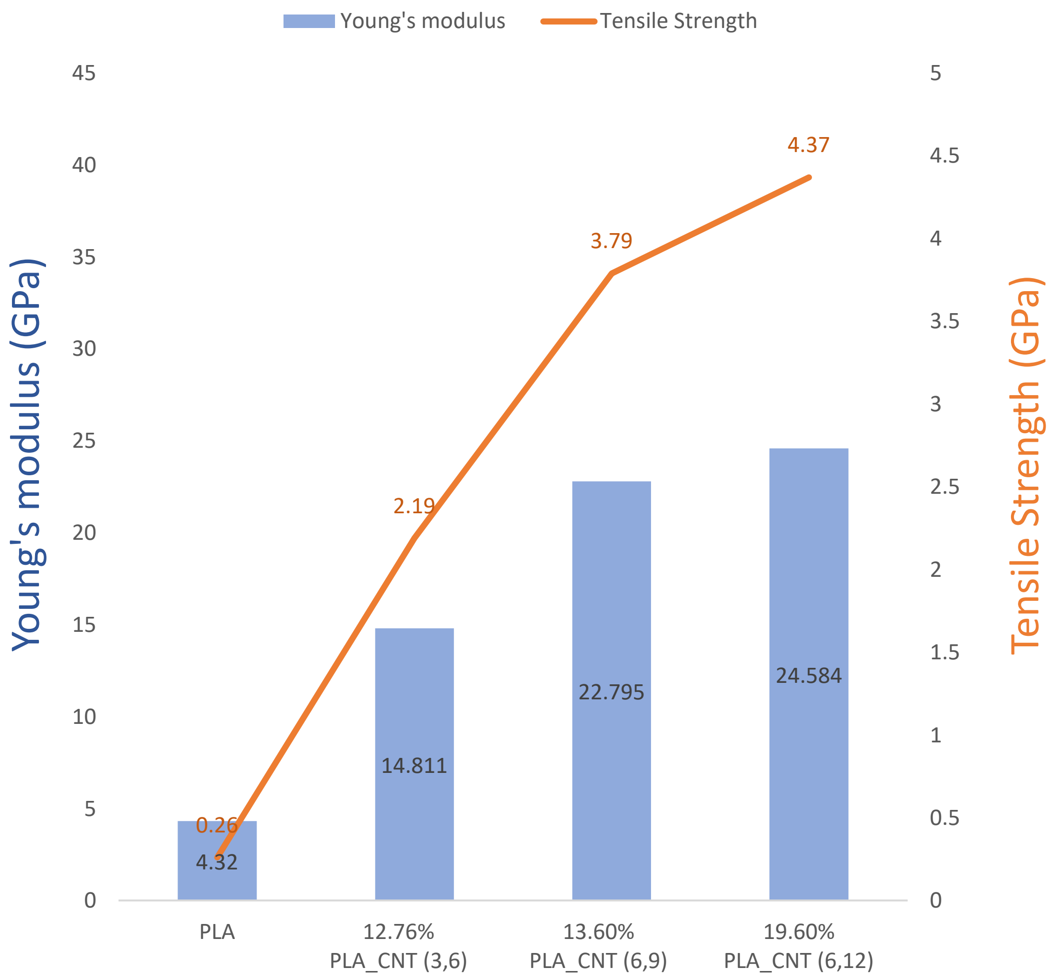
Result Comparison



Composition	Volume Fraction	Tensile strength (GPa)	Young's modulus (GPa)
PLA-SWNT (3,6)	12.76%	2.19	14.811
PLA-SWNT (6,9)	13.60%	3.79	22.795
PLA-SWNT (6,12)	19.60%	4.37	24.584

Result and Analysis

Discussion



Composition	Volume Fraction	Tensile strength (GPa)	Young's modulus (GPa)
PLA	N/A	0.26	2.085
PLA-SWNT (3,6)	12.76%	2.19	14.811
PLA-SWNT (6,9)	13.60%	3.79	22.795
PLA-SWNT (6,12)	19.60%	4.37	24.584

- Increase in tensile strength is 8.4 to 16.8 times
- Increase in Young's modulus is 7.1 to 11.79 times
- This indicates enhancement of mechanical property in terms of young's modulus and tensile strength when the PLA is reinforced with Carbon nanotube

Conclusion

Conclusion and Recommendation

- Performing uniaxial tensile deformation using MD simulation
- CNT reinforcement in PLA enhanced it’s mechanical properties
  - Tensile strength from 8.4 to 16.8 times
  - Young’s modulus from 7.1 to 11.79 times
- Result indicates increase in load carrying capacity

- Thermal and electrical properties are yet to be explored
- Implementing this composite as replacement to PLA in 3D printing technology and medical use
- Cost of CNT and reinforcement against improvement is a consideration
- Optimal ratio is the key to sustain this improvement

Reference

- A Shakoor, R Muhammad, N L Thomas and V V Silberschmidt ‘Mechanical and thermal characterisation of poly (l-lactide) composites reinforced with hemp fibres’ Journal of physics: Conference Series 451 (2013) 012010
- Anders Sodergard, Mikael Stolt, ‘Properties of lactic acid-based polymers and their correlation with composition' Prog. Polym. Sci. 27 (2002) 1123–1163.
- Ajayan, P.M., Stephan, O., Colliex, C. and Trauth, D. (1994) ‘Aligned carbon nanotubes arrays formed by cutting a polymer resin-nanotube composite’, Science, Vol. 256, No. 5176, pp.1212–1214.
- A.J. Lasprilla, G.A. Martinez, B.H. Lunelli, A.L. Jardini, R.M. Filho, ‘Poly-lactic acid synthesis for application in biomedical devices — A review’ Biotechnol. Adv. 30 (2012) 321–328
- Carolina Gonçalves, InêsC. Gonçalves, FernãoD. Magalhãesand Artur M. Pinto (2017) ‘Poly (lactic acid) Composites Containing Carbon-Based Nanomaterials: A Review’ Polymers, Volume 9, Issue 7 (July 2017)
- Chandra B, Bhattacharjee J, Purewal M, Son YW, Wu Y, Huang M, Yan H, Heinz TF, Kim P, Neaton JB, Hone J (2009), ‘Molecular-scale quantum dots from carbon nanotube heterojunctions. Nano Lett, 9, 1544.

Reference

- D.E. Henton, P. Gruber, J. Lunt, J. Randall, in: A.K. Mohanty, M. Misra, L.T. Drzal (Eds.), Natural Fibers, Biopolymers, and Biocomposites, Taylor & Francis, F.L. Boca Raton 2005, pp. 527–577.
- Dauber-Osguthorpe, P.; Roberts, V. A.; Osguthorpe, D. J.; Wolff, J.; Genest, M.; Hagler, A. T. ``Structure and energetics of ligand binding to proteins: *E. coli* dihydrofolate reductase-trimethoprim, a drug-receptor system'', *Proteins: Structure, Function and Genetics*, 4, 31-47 (1988)
- Dewei Qi, Jeffrey A. Hinkley, Gouwei He (2005) 'Molecular dynamics simulation of thermal and mechanical properties of polyimide–carbon-nanotube composites'Modelling and Simulation in Materials Science and Engineering 13(4):493 · April 2005
- Ebbesen TW, Lezec HJ, Hiura H, Bennett JW, Ghaemi HF, Thio T (1996), 'Electrical conductivity of individual carbon nanotubes. Nature, 382, 54.
- Evgeni Ivanov, RumianaKotsilkova, HeshengXia, YinghongChen, Ricardo K. Donato, Katarzyna Donato, Anna Paula Godoy, Rosa Di Maio,Clara Silvestre, SossioCimminoand VerislavAngelov(2019) 'PLA/Graphene/MWCNT Composites with Improved Electrical and Thermal Properties Suitable for FDM 3D Printing Applications' Appl. Sci., Volume 9, Issue 6 (March-2 2019)
- Farah, Shady, et al. "Physical and Mechanical Properties of PLA, and Their Functions in Widespread Applications — A Comprehensive Review." Advanced Drug Delivery Reviews, vol. 107, Dec. 2016, pp. 367–92.

Reference

- *Garlotta, Donald (2001). "A Literature Review of Poly (Lactic Acid)". Journal of Polymers and the Environment. 9 (2): 63–84*
- Hagler, A. T.; Dauber, P.; Lifson, S. (1979) ``Consistent force field studies of intermolecular forces in hydrogen bonded crystals. III. The C=OH-O hydrogen bond and the analysis of the energetics and packing of carboxylic acids", *J. Am. Chem. Soc*., **101**, 5131-5141.
- Han, Y. and Elliott, J. (2007) ‘Molecular dynamics simulation of the elastic properties of polymer/carbon nanotube composites’, Computational Material Science, Vol. 39, No. 2, pp.315–323.
- Hua Wang, Xiushi Sun, Paul Seib (2002) ‘Mechanical Properties of Poly(lactic Acid) and Wheat Starch Blends with Methylenediphenyl Diisocyanate’; Journal of Applied Polymer Science, Vol. 84, 1257–1262
- Ijima, S. (1991) ‘Helical microtubules of graphitic carbon’, Nature, Vol. 354, No. 6348, pp.56–58.
- Jin Tae Yoon, Young Gyu Jeong, Sang Cheol Lee, Byung Gil Min, (2008) ‘Influences of poly(lactic acid)-grafted carbon nanotube on thermal, mechanical, and electrical properties of poly(lactic acid)’, Polymers for Advanced Technologies 20(7):631 - 638 · July 2009
- M. S. Z. Mat Desa, A. Hassan, A. Arsad and N. N. B. Mohammad ‘Mechanical properties of poly(lactic acid)/multiwalled carbon nanotubes nanocomposites’ Materials Research Innovations 2014 VOL 18

Reference

- Ruoff RS, Tersoff J, Lorents DC, Subramoney S, Chan B. (1993), 'Radial deformation of carbon nanotubes by van der Waals forces. Nature, 364, 514.
- Ruoff RS, Lorents DC (1995), 'Mechanical and thermal properties of carbon nanotubes. Carbon', 33, 925.
- Sun, H. (1995) 'Ab initio calculations and force field development for computer simulation of polysilanes', Macromoloecules, Vol. 28, No. 3, p.701.
- Sun, H. (1998) 'COMPASS: an ab-initio force-field optimized for condensed-phase applications – overview with details on alkene and benzene compounds', Journal of Physical Chemistry B, Vol. 102, No. 38, pp.7338–7364.
- Sun, H., Ren, P. and Fried, J.R. (1998) 'The COMPASS force field: parameterization and validation for phosphazenes', Computational and Theoretical Polymer Science, Vol. 28, Nos. 1–2, pp.229–246.
- Suthaphat Kamthai, and Rathanawan Magaraphan (2016) 'Thermal and mechanical properties of polylactic acid (PLA) and bagasse carboxymethyl cellulose (CMCB) compositeby adding isosorbide diesters', AIP Conference Proceedings 1664, 060006;
- Sandeep B. Sane, TcaginCagin, Wolfgang G. Knauss, William A. Goddard (2001),'Molecular dynamics simulations to compute the bulk response of amorphous PMMA' Journal of Computer-Aided Materials Design 8(2):87-106
- Södergård, Anders; Mikael Stolt (2010). "3. Industrial Production of High Molecular Weight Poly (Lactic Acid)". In Rafael Auras; Loong-Tak Lim; Susan

Reference

- E. M. Selke; Hideto Tsuji (eds.). Poly (Lactic Acid): Synthesis, Structures, Properties, Processing, and Applications. pp. 27–41

- Waldman, Marvin; Hagler, A.T. (September 1993). "New combining rules for rare gas van der waals parameters". *Journal of Computational Chemistry*. 14 (9): 1077–1084.

- X. Zhao and L. Ye (2011) “Structure and mechanical properties of polyoxymethylene/multi-walled carbon nanotube composites,” Compos. Part B Eng., vol. 42, no. 4, pp. 926–933.

- Yu MF, Lourie O, Dyer MJ, Moloni K, Kelly TF, Ruoff RS (2000), ‘Strength and breaking mechanism of multiwalled carbon nanotubes under tensile load’. Science, 287, 637.

THANK YOU