

Determining Mechanical properties of Poly Vinyl Alcohol using Molecular Dynamics

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Abstract

Polyvinyl alcohol (PVA) is a non-toxic, thermoplastic polymer known for its biodegradability and versatile mechanical properties. This study aims to explore the mechanical characteristics of PVA, using molecular dynamics simulations. In the realm of biomedical applications, PVA hydrogels act as supportive frameworks for tissue engineering, owing to their biocompatibility and customizable mechanical properties. By manipulating hydration levels, scientists can fine-tune these hydrogels to mimic natural tissues, thereby fostering cell proliferation and tissue restoration. By managing hydration levels during production, manufacturers can tune the mechanical strength and resilience of these films, ensuring the longevity and robustness of packaged products.

Our objective encompasses conducting a tensile test under a constant strain rate through molecular dynamics simulation using LAMMPS, generating stress-strain plots and fitting them with established viscoelastic models to ascertain model parameters. Additionally, we aim to identify viscoelastic properties such as G (stress relaxation function) using constant strain rate tests. Moreover, properties like Y and strength diminish significantly with increased hydration. This variation is instrumental in crafting PVA with tailored mechanical attributes by adjusting water percentage, especially for biomaterials aiming to mimic biological tissues.

Hence, this investigation bears significance in optimizing PVA's mechanical characteristics to align with diverse applications across various industries.

Introduction

Molecular Dynamics (MD) is a computational simulation technique employed in various scientific disciplines to investigate the behaviour and properties of molecular systems at the atomic level. Molecular Dynamics (MD) simulations function by numerically integrating Newton's equations of motion to predict the time evolution of a molecular system. At the core of MD lies the principle that the behaviour of a system can be determined by tracking the positions and velocities of its constituent atoms or molecules over time. Initially, an MD simulation requires the specification of an

initial atomic configuration and the assignment of velocities according to a chosen temperature distribution, often based on the Maxwell-Boltzmann distribution. Subsequently, the forces acting on each atom are calculated based on interatomic potentials or force fields that describe the interactions between atoms. These potentials account for various types of interactions, including bond stretching, angle bending, and non-bonded interactions such as van der Waals forces and electrostatic interactions. By iteratively updating the positions and velocities of atoms using numerical integration schemes such as the Verlet algorithm, MD simulations enable the

prediction of the system's trajectory over time. Through the analysis of these trajectories, researchers can gain insights into structural changes, thermodynamic properties, and mechanical behaviour, providing valuable information for understanding the properties of materials like Polyvinyl Alcohol (PVA) at the molecular level.

Understanding the mechanical behaviour of PVA at the molecular level is crucial for tailoring its properties to specific applications. Traditional experimental techniques often face challenges in providing detailed insights into molecular interactions and dynamics. This is where MD simulations offer significant advantages. By numerically solving Newton's equations of motion for a system of interacting atoms or molecules, MD enables researchers to explore the intricate structural changes and mechanical responses of polymer materials under various conditions.

Methods

1. **Model building:** Materials Studio was utilized to create the model.

PVA is a linear polymer with the formula $[\text{CH}_2\text{CH}(\text{OH})]_n$. Using Materials Studio 2020, polymeric chains of length n were constructed. Packmol facilitated the packing of 50 such chains along with a specified percentage of water molecules (20%). The resulting data was stored in a PDB file format. PDB files contain coordinates, atom types, and bond lists for each atom. Subsequently, VMD was employed to generate a LAMMPS file.

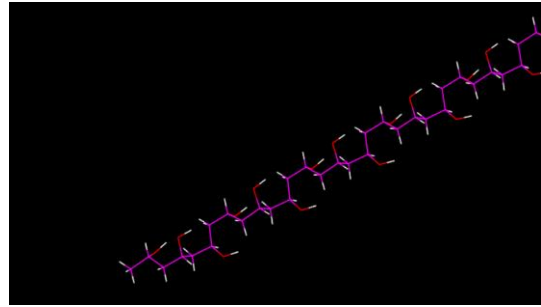
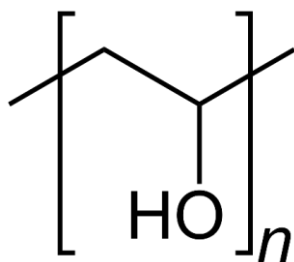


Fig 1. Materials Studio: Structure of PVA

In the LAMMPS file, specifications typically include:

a) **Atom Types Force Field parameters:**

In Molecular Dynamics (MD), a force field is a set of mathematical functions and parameters used to describe the interactions between atoms and molecules within a system. These interactions include bonded interactions (such as bonds, angles, and dihedrals) and non-bonded interactions (such as van der Waals forces and electrostatic interactions).

Here we adopted AMBER force field [1]. Total energy of the system is given by:

$$E_{\text{total}} = \sum_{\text{bonds}} K_r (r - r_{\text{eq}})^2 + \sum_{\text{angles}} K_{\theta} (\theta - \theta_{\text{eq}})^2 + \sum_{\text{dihedrals}} \frac{V_n}{2} [1 + \cos(n\phi - \gamma)] + \sum_{i < j} \left[\frac{A_{ij}}{R_{ij}^{12}} - \frac{B_{ij}}{R_{ij}^6} + \frac{q_i q_j}{\epsilon R_{ij}} \right]$$

The FF parameters include all the constants mentioned in the equation.

The atom typing includes:

- CT1 – sp³ carbon (CH₂) without -OH group
- CT2 – sp³ carbon (CH) attached with -OH group
- H1 – H attached to CT2 carbon
- HC – H attached to CT1
- HO – H attached to alcohol
- HW – H in water
- OH – O in the -OH
- OW – O in water

- b) **Simulation Box Dimensions:** The dimensions of the simulation box are -300 300 A in all three directions (cubic).
- c) **Atom Coordinates:** The LAMMPS file includes the coordinates of each atom in the system. These are often read from the PDB file generated earlier.
- d) **Bond and Angle Information:** The LAMMPS file specifies the bonds and angles between atoms based on the connectivity information from the PDB file.
- e) **Parameters:**
Includes all the bond, angle and dihedral parameters defined by
 Bond_coeff - $K_r r_{eq}$
 Angle_coeff - $K_\theta \theta_{eq}$
 Pair_Coeff - $\sigma_{ij} \epsilon_{ij}$
 Dihedral_coeff - $V_n n \gamma$

for all bonded (2-body, 3-body and 4-body and non – bonded interactions)

2. Minimisation and Equilibration

```
#Initial_settings
units          real
boundary       p p p
atom_style     full
log            log_equilibration.txt

#Styles
special_bonds  amber
bond_style     harmonic
angle_style    harmonic
dihedral_style charmm
pair_style     lj/cut/coul/long 10.0
kspace_style   pppm 1.0e-3
```

We commence by establishing the units as real, aligning with those specified in the LAMMPS documentation. The boundary conditions are set to periodic, denoted by the style "p," allowing particles to interact seamlessly across boundaries, potentially exiting one end of the box and entering from the opposite end. A periodic dimension might alter in size due to

constant pressure boundary conditions or box deformation. The computation of long-range Coulombic interactions or $1/r^6$ interactions resulting from periodic boundary conditions can be computationally intensive, and thus, it is approximated using methods like Ewald or particle-particle-particle mesh solver.

```
# Initial_settings
variable itr equal 100000 #
iterations
velocity all create 300.0 4928459
mom yes dist gaussian
compute c1 all gyration
thermo_style custom step pe temp
press density c_c1
thermo $(v_itr/10)

#Minimisation
thermo 100
min_style cg
minimize 1.0e-5 1.0e-5 1000 1000
thermo $(v_itr/10)

#NPT
fix Ef all npt temp 300 300 50 iso
1 1 1000
run $(v_itr)
unfix Ef
```

“Thermo_style” command is used to customise the information to be printed, here we need the temperature, pressure and density to be printed after every itr/10 timesteps.

Minimised using conjugate gradient with tolerance of 1.0e-5 and max no. of iterations is 500.

We conduct an NPT fix where the temperature is kept constant at 300K, and the pressure is regulated to 1 bar by the end of the fix. The term "iso" signifies that pressure is uniform across all faces of the box. Once this process is completed, our model is expected to have reached equilibrium and is prepared for further work.

3. Tensile test simulation

The model is deformed in z-direction at a constant rate i.e. the z varies with time as $z = z_0 + v \cdot t$. Here, v refers to the velocity rate at which we deform z -length which is

written in terms of initial box length using the variable 'z_initial_static'. We have to use an NPT fix to maintain 0 pressure in the other two direction. One significant drawback of using a scaled-down model is the necessity for exceptionally high levels of strain to achieve stable results. Here our strain rate is 10^{10} .

```
variable z_initial_dynamic equal lz
variable z_initial_static equal ${z_initial_dynamic}
fix T1 all deform 1 z vel $(1*v_z_initial_static/v_itr)
fix T2 all npt temp 300.0 300.0 100.0 x 0.0 0.0 1000.0 y 0.0 0.0 1000.0 drag 2
run 100000
```

Results and Discussions

1. Minimisation stats

```
Minimization stats:
Stopping criterion = energy tolerance
Energy initial, next-to-last, final =
2124461.89705661
671020.404736052
671019.413014248
Force two-norm initial, final =
79713.265 172.44175
Force max component initial, final =
738.66811 41.701863
Final line search alpha, max atom move =
0.0016777541 0.06996547
Iterations, force evaluations = 75 127
```

- The variation of Potential Energy, density, pressure with respect to time during the equilibration are shown below:

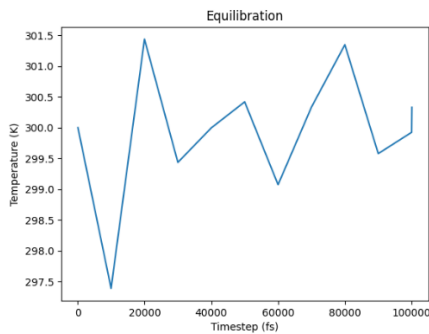


Fig 2.

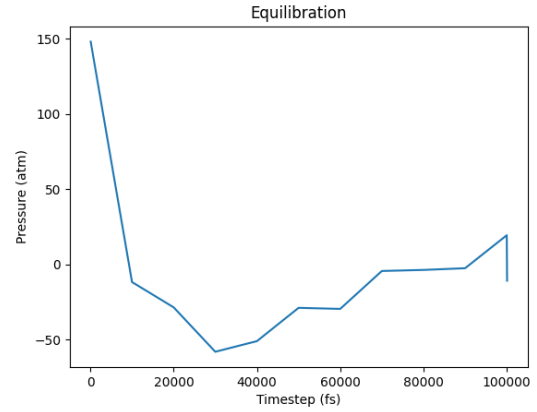


Fig 3.

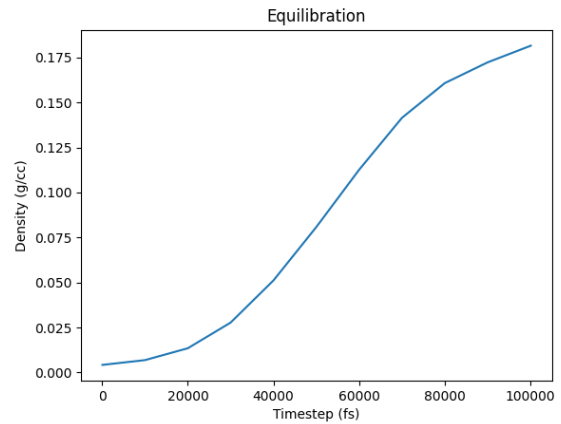


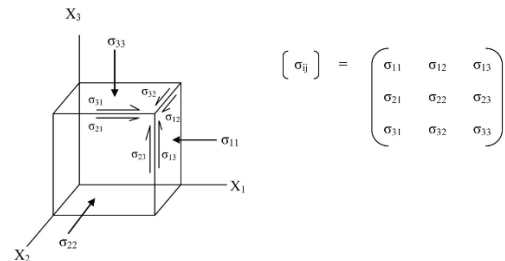
Fig 4.

The temperature and pressure are fluctuating and gradually reaching 300K and 1atm. Density keeps increasing. Ideally it should reach 1g/cc but due to lesser number of iterations it hasn't reached that density.

3. Stress vs Strain

a. Youngs Modulus

Since we only have r and v of all the particles, we are finding stress in terms of r and v using Virial's theorem:



$$P_{IJ} = \frac{1}{V} \sum_{k=1}^N m_k v_{kI} v_{kJ} + \frac{1}{V} \sum_{k=1}^{N'} r_{kI} f_{kJ}.$$

Where we find the stress tensor components using the r and v data.

Since the load is applied only in the z direction, all the other components are zero except for P_{zz} . Now Stress is plotted against strain using Matplotlib, python. The slope of the initial section of the graph gives us the Youngs Modulus.

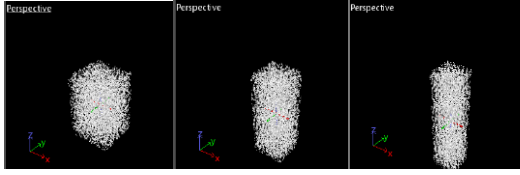


Fig 5. Snaps at $t = 0$, $t = 50,000$ timesteps and $t = 1,00,000$ timesteps

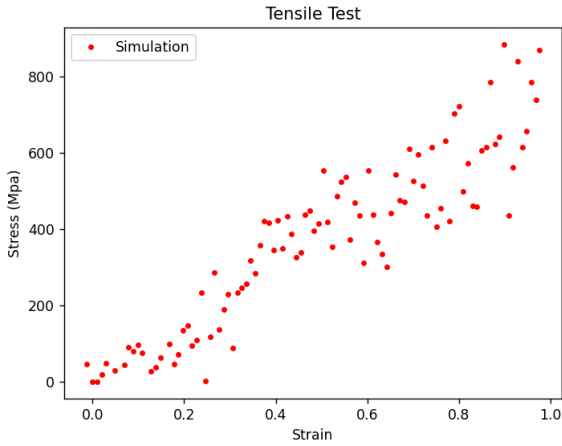


Fig 6. Tensile deformation until 1.0 Strain

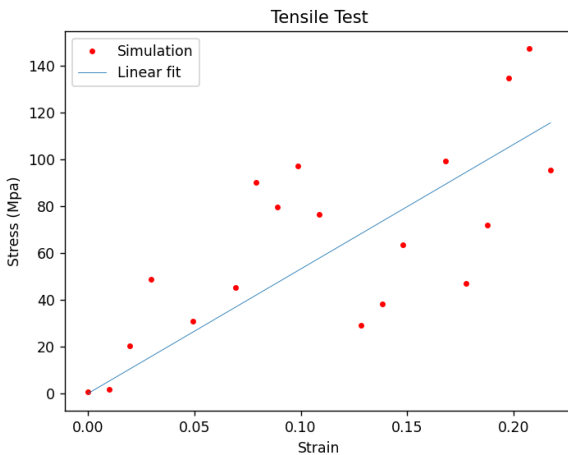


Fig 7. Scanning into the linear region (until 0.2 strain) and fitting

Youngs Modulus (by Least RMS error fit): 531.55 MPa. This is in correspondence with experimental Y modulus of PVA which is around 500 – 700 Mpa.

b. Viscoelastic properties

Viscoelastic behavior is a property exhibited by certain materials that display both viscous (flow-like) and elastic (recovery-like) characteristics when subjected to stress or deformation. Unlike purely elastic materials, which deform instantaneously and fully recover their original shape when the stress is removed, or purely viscous materials, which deform continuously under stress, viscoelastic materials exhibit a combination of both behaviors. Materials like PVA, exhibit this behaviour.

When a viscoelastic material is subjected to a constant strain, it initially deforms like an elastic material, but over time, it also exhibits viscous flow, leading to a gradual relaxation of stress. This relaxation process occurs due to the rearrangement of molecular chains or other structural elements within the material. The stress relaxation modulus G is expressed as

$$G(t) = \frac{\sigma(t)}{\epsilon_0}$$

The function $G(t)$ is the stress per unit of applied strain and is termed Stress Relaxation.

c. General expression for G

Mechanical analogs are one-dimensional structures which are assembled using basic structural elements: the linear spring and linear damper. A variety of mechanical analogs have been developed to capture the nature of viscoelastic solids and fluids such as Maxwell, Kelvin-Voigt, 3-Parameter and 4 parameter models. A generalized approximation for stress relaxation is given by the Prony series.

$$G(t) = G_0 + G_1 e^{\frac{-t}{\tau_1}} + G_2 e^{\frac{-t}{\tau_2}} + G_3 e^{\frac{-t}{\tau_3}} \dots + G_N e^{\frac{-t}{\tau_N}}$$

Where G_i, τ_i are all constants.

d. How to find G from constant strain rate test?

When the strain rate is α then $G(t) = \frac{1}{\alpha} * d\sigma/dt$. We can assume a generalized prony series expression for G and find all the constants associated with the expression by solving it using numerical methods using the stress vs time data we have got. Since our simulation ran for a fewer number of iterations we couldn't fit properly.

Conclusion

We have systematically seen how to simulate the deformation behaviour of polymers using Molecular Dynamics. Here we have simulated PVA molecules with 20% hydration and subjected to tensile test. And with the Stress v Strain plot obtained Y modulus was found out to be 531.55 MPa and matched with the general Y of the PVA system.

Future Work

- We can use Supercomputers to run for higher no. of iterations get a more reliable result and therefore find G .
- Study the effect of crosslinking.
- Simulate sinusoidal strain to find G' (loss modulus) and G'' (storage modulus).

Acknowledgement

Patel Krish performed the packing of molecules. Anushka V and Vignesh G (working on the same project with different levels of hydration) helped me to write the input files and parameters file.

References

- [1] Wendy D. Cornel, "A Second Generation Force Field for the Simulation of Proteins, Nucleic Acids, and Organic Molecules".
- [2] Yan Tang, Zechuan Yu, Lik-ho Tam, Ao Zhou, D.M. Li, "Behavior of water molecules in polyvinyl alcohol gel amid stretch and temperature changes": A molecular dynamics study, Materials Today Communications.
- [3] Lujuan Li et. al, "Water governs the mechanical properties of poly(vinyl alcohol)", Polymer.