Supporting Information

Comparative Role of Chain Scission and Solvation in the Biodegradation of Polylactic Acid (PLA)

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SI1) Principle and property estimation from dynamic nanoindentation

Viscoelastic material can be modelled by two basic elements: the spring and a dashpot. Each element is assigned a material constant. Elastic Modulus (E_i) and viscosity (η_i). The mechanical model for dynamic nanoindentation (NanoDMA) can be depicted as in Figure 1 in which K_f is the frame stiffness, K_i is the support spring stiffness, D_i stands for indenter damping and m_i for indenter mass. S and D_S are unknown stiffness and damping coefficients for tested material.

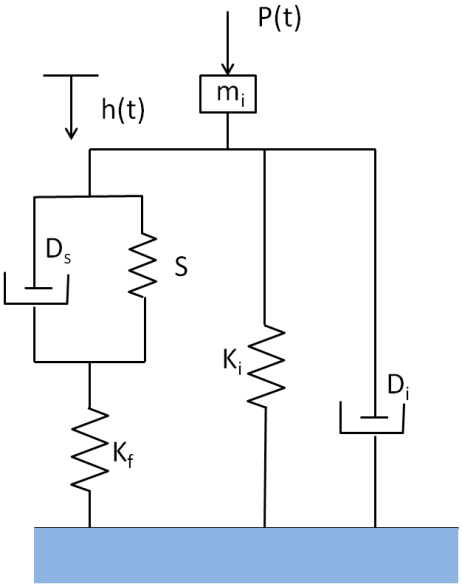

Figure S1: Schematic of the set up for Dynamic Nanoindentation (nanoDMA)

It is usually assumed that the load frame stiffness K_f provides the major contribution to the total stiffness such that $K_f \rightarrow \infty$. Then, such a system can be described by the equation of motion (force balance equation) as:

$$P(t) = m_i\ddot{h} + (D_i + D_s)\dot{h} + (K_i + S)h$$

The relation between force P and displacement h is called the transfer function. An analytical solution of this differential equation can be found as follows:

$$TF = \frac{P(t)}{h(t)} = (K_i + S - m_i\omega^2) + i(D_i + D_s)\omega$$

The magnitude and phase angle of transfer function are given by:

$$|TF| = \sqrt{(K_i + S - m_i\omega^2)^2 + \left((D_i + D_s)\omega\right)^2}$$

$$\tan\varphi = \frac{(D_i + D_s)\omega}{K_i + S - m_i\omega^2}$$

The real and imaginary part of the transfer function represent the storage (E') and the loss (E") moduli of the system.

$$E' = K_i + S - m_i\omega^2$$

$$E" = (D_i + D_s)\omega$$

From the equations of contact the storage and loss moduli of the sample can be described as follows:

$$E' = \frac{S\sqrt{\pi}}{2\beta\sqrt{A}}$$

$$E" = \frac{\omega D_s\sqrt{\pi}}{2\beta\sqrt{A}}$$

and the phase lag tan δ for the sample as:

$$\tan\delta = \frac{\omega D_s}{S}$$

SI2.1) Forcefield Parameters

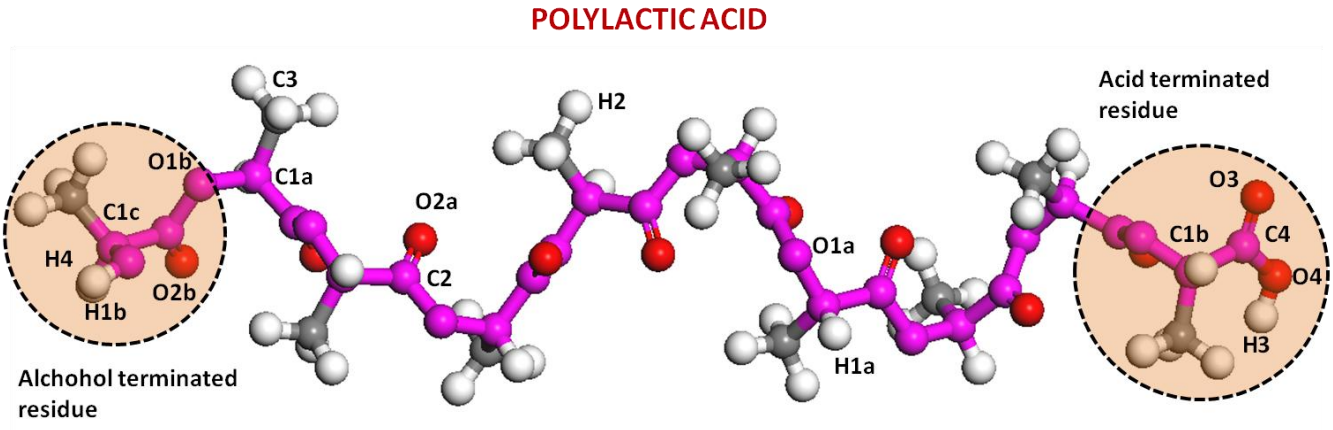

Figure S2.1.1: Structure of PLA

Atom Types in PLA

Atom Name (Mass)	Description	Partial Charge
C1a 12.011	Carbon part of -CH- (Repeat Unit)	0.22
C1b 12.011	Carbon part of –CH-COOH (Acid terminated residue)	0.11
C1c 12.011	Carbon part of –CH-OH (Alcohol terminated residue)	0.425
C2 12.011	Carbon part of -(C=O)- (Repeat Unit)	0.52
C3 12.011	Carbon part of CH_3 (Repeat Unit)	-0.18
C4 12.011	Carbon part of –COOH (Acid terminated residue)	0.52
O1a 15.9994	Oxygen part of -O-(C=O)-CH- (Repeat Unit)	-0.34
O1b 15.9994	Oxygen part of -O-(C=O)-CH-OH (Alcohol terminated residue)	-0.33
O2a 15.9994	Oxygen part of -O-(C=O)-CH- (Repeat Unit)	-0.43
O2b 15.9994	Oxygen part of -O-(C=O)-CH-OH (Alcohol terminated residue)	-0.44
O3 15.9994	Oxygen part of -(C=O)-OH (Acid terminated residue)	-0.53

O4 15.9994	Oxygen part of -(C=O)-OH (Acid terminated residue)	-0.44
O5 15.9994	Oxygen part of -CH-OH (Alcohol terminated Residue)	-0.683
H1a 1.008	Hydrogen part of –CH- (Repeat Unit, Acid terminated residue)	0.03
H1b 1.008	Hydrogen part of –CH- OH (Alcohol terminated Residue)	0.09
H2 1.008	Hydrogen part of –CH3 (Repeat Unit)	0.06
H3 1.008	Hydrogen part of –COOH (Acid terminated residue)	0.31
H4 1.008	Hydrogen part of -CH-OH (Alcohol terminated Residue)	0.418

The forcefield equation can be represented as follows:

$$E_{total} = E_{bond} + E_{angle} + E_{dihedral} + E_{van\ der\ Waals} + E_{electrostatic}$$

a) Bond parameters

$$E_{bond} = K_b(r - r_0)^2$$

Atom i	**Atom j**	**r^0_{ij} (Å)**	**K^b_{ij} (kcal/mol Å^2)**
C2	C1a	1.2890	160
C2	C1c	1.2890	160
C2	O2a	1.1110	126
C2	O2b	1.1110	126
O1a	C2	1.0950	70
O1b	C2	1.0950	70
C1a	C3	1.1070	75
C1b	C3	1.1070	75
C1c	C3	1.1070	75
C1a	H1a	1.0950	100
C1b	H1a	1.0950	100
C1c	H1b	1.0950	100

C3	H2	1.0950	100
C1a	O1a	1.0780	66
C1b	O1a	1.0780	66
C1a	O1b	1.0780	66
C1c	O5	1.0950	70
H3	O3	1.2340	166
H4	O5	1.2340	166
C4	O3	1.0884	166
C4	C1b	1.1304	162
C4	O4	1.0558	100
C1c	O5	1.095	70
C2	C1c	1.289	160
C1a	O1a	1.078	66
C1c	C3	1.107	75
C1a	H1a	1.095	100
C1b	O1a	1.078	66
C1b	H1a	1.095	100
C2	O2b	1.111	126
H4	O5	1.234	166
C3	H2	1.095	100
C2	C1a	1.289	160
C1c	H1b	1.095	100
C1a	C3	1.107	75
C1b	C3	1.107	75
O1a	C2	1.095	70
C4	C1b	1.1304	162
H3	O3	1.234	166
C1a	O1b	1.078	66
C2	O2a	1.111	126

O1b	C2	1.095	70
C4	O3	1.0884	166

b) Angle parameters

$$E_{angle} = K_\theta(\theta - \theta_0)^2$$

Atom i	**Atom j**	**Atom k**	**θ_{0ijk}(degrees)**	**K^{θ}_{ijk} (kcal/mol rad^2)**
C1c	C2	O1b	128.90	160
H1	C1b	O1	109.50	70
C1b	C4	O3	108.00	140
C2	C1c	O5	108.50	110
C1b	C4	O4	120.40	160
C2	C1	O1	105.58	100
C1	O1	C2	108.84	166
C2	C1c	C3	111.10	126
C2	C1	H1	109.50	70
C3	C1	O1	109.50	100
H2	C3	H2	107.80	66
C3	C1	H1	110.70	75
C1b	O1	C2	108.84	166
C3	C1b	C4	111.10	126
C3	C1	O1b	109.50	100
C1	C3	H2	110.70	75
C4	O3	H3	113.00	70
C4	C1b	O1	109.50	100
H1b	C1c	O5	109.50	70
O1	C2	O2	123.40	166
C4	C1b	H1	109.50	70

C1b	C3	H2	110.70	75
C1c	C3	H2	110.70	75
C1c	C2	O2b	128.90	160
C2	C1c	H1b	109.50	70
C1c	O5	H4	108.50	110
H1	C1	O1b	109.50	70
C2	C1	C3	111.10	126
C3	C1c	H1b	110.70	75
C3	C1c	O5	109.50	100
C1	C2	O1	113.04	162
O1b	C2	O2b	123.40	166
C1	C2	O2	128.90	160
C2	C1	O1b	105.58	100
C1	O1b	C2	108.84	166
C3	C1b	O1	109.50	100
O3	C4	O4	113.00	70
H1	C1	O1	109.50	70
C3	C1b	H1	110.70	75

c) Dihedral parameters

$$\boldsymbol{E_{dihedral}} = \sum_{\boldsymbol{n=1-4}} \boldsymbol{A_n cos^{n-1}(\varphi)}$$

Atom i	**Atom j**	**Atom k**	**Atom l**	**A1 (kcal/mol)**	**A2 (kcal/mol)**	**A3 (kcal/mol)**	**A4 (kcal/mol)**
O5	C1c	C2	O2b	0	0	0	0
H1	C1b	O1	C2	0.098999	-0.297	0	0.395999
H1	C1	C3	H2	0.15	-0.45	0	0.600001
C3	C1c	C2	O2b	0.742501	0.902501	-1.228	-1.388

O1	C1b	C3	H2	0.233999	-0.702	0	0.936
H1b	C1c	C2	O1b	0.066002	-0.198	0	0.264001
O2	C2	O1	C1b	5.124004	0	-5.124	0
C4	C1b	C3	H2	-0.05	0.15	0	-0.2
C1	C2	O1	C1	0	0	0	0
C1	C2	O1	C1b	0	0	0	0
C2	C1	O1b	C2	0.41	-0.68	0.25	1.340001
H1b	C1c	C3	H2	0.15	-0.45	0	0.600001
H1b	C1c	O5	H4	0.225	-0.675	0	0.900001
H1b	C1c	C2	O2b	0	0	0	0
O1b	C1	C2	O1	-0.275	-0.275	0	0
O1b	C1	C2	O2	0	0	0	0
C3	C1b	C4	O3	1.271	-0.175	-0.546	0.900001
C3	C1b	C4	O4	0.546	0	-0.546	0
H1	C1b	C3	H2	0.15	-0.45	0	0.600001
C2	C1c	C3	H2	-0.038	0.114001	0	-0.152
C2	C1c	O5	H4	-0.106	-0.916	0.173999	0.984
O1	C1b	C4	O3	0	0	0	0
O1	C1b	C4	O4	0	0	0	0
O1	C1	C2	O1	-0.275	-0.275	0	0
C3	C1	O1b	C2	-0.525	-1.243	0.126002	0.844002
C1b	C4	O3	H3	6.250007	0.750001	-5.50001	0
O2	C2	O1	C1	5.124004	0	-5.124	0
O1	C1	C2	O2	0	0	0	0
C2	C1	O1	C2	0.41	-0.68	0.25	1.340001
C3	C1	C2	O1	-0.2765	0.829501	0	-1.106
C3	C1	C2	O2	0.742501	0.902501	-1.228	-1.388
C3 135	C1b	O1	C2	-0.525	-1.243	0.126002	0.844002
H1	C1	C2	O1	0.066002	-0.198	0	0.264001

C1c	C2	O1b	C1	0	0	0	0
H1	C1	C2	O2	0	0	0	0
C3	C1c	O5	H4	-0.106	-0.916	0.173999	0.984
O1b	C1	C3	H2	0.233999	-0.702	0	0.936
C3	C1	O1	C2	-0.525	-1.243	0.126002	0.844002
H1	C1b	C4	O3	0	0	0	0
H1	C1b	C4	O4	0	0	0	0
H1	C1	O1	C2	0.098999	-0.297	0	0.395999
O4	C4	O3	H3	5.500006	0	-5.50001	0
C2	C1	C3	H2	-0.038	0.114001	0	-0.152
C4	C1b	O1	C2	0.41	-0.68	0.25	1.340001
O5	C1c	C2	O1b	-0.275	-0.275	0	0
O5	C1c	C3	H2	0.233999	-0.702	0	0.936
O1	C1	C3	H2	0.233999	-0.702	0	0.936
H1	C1	O1b	C2	0.098999	-0.297	0	0.395999
C3	C1c	C2	O1b	0	0	0	0
O2b	C2	O1b	C1	5.124004	0	-5.124	0

c) van der Waals

$$E_{van\ der\ Waals} = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

Atom Name	**σ_i (Å)**	**ε_i (kcal/mol)**
C1a	4.05359	0.02
C1b	4.05359	0.02
C1c	4.05359	0.02
C2	3.75000	0.105
C3	3.50000	0.066
C4	3.75000	0.105

O1a	3.15378	0.1521
O1b	3.15378	0.1521
O2a	2.96000	0.21
O2b	2.96000	0.21
O3	3.00000	0.17
O4	2.96000	0.21
O5	3.12000	0.17
H1a	2.42000	0.015
H1b	2.42000	0.015
H2	2.50000	0.3
H3	0	0
H4	0	0

Water Molecule (TIP3P water model)

Figure S2.1.2: Structure of Water

LJ potential: Hw σ=0.4000 Å; ε = 0.0460 kcal/mol

Ow σ=3.1507 Å; ε = 0.1521 kcal/mol

Bond coefficient

Hw-Ow: K_b=450 kcal/mol Å^2

r_0= 0.9572 Å

Angle Coefficient

Hw-Ow-Hw: K_θ=55 kcal/mol rad^2

θ_0= 104.52^0

Hydroxyapatite (HAp)

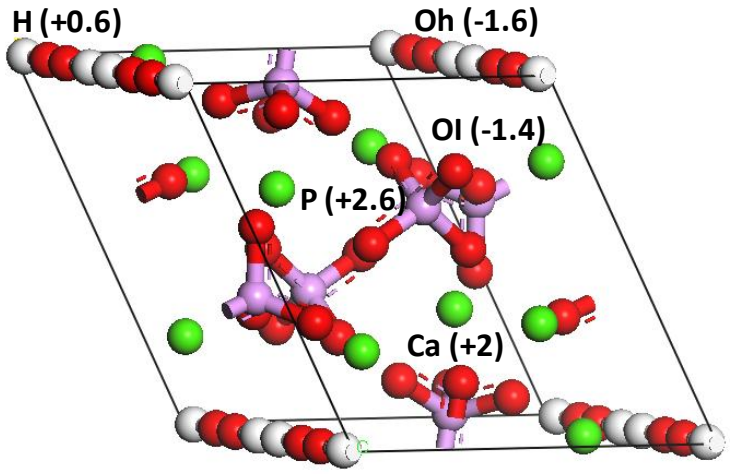

Figure S2.1.3: Structure of HAp

The lattice parameters for a single unit cell of HAp are as follows:

Lattice Parameters

a	b	c	α	β	γ
9.424 Å	9.424 Å	6.879 Å	90^0	90^0	120^0

A single HAp nanoparticle used in the simulation is a 3x3x3 replication of the unit cell. Thus the size of the nanoparticle is 28.27 Å × 28.27 Å × 20.637 Å.

LJ potential: P σ=3.48565 Å; ε = 0.97406 kcal/mol

OI σ=3.03254 Å; ε = 0.25201 kcal/mol

Ca σ=2.94133 Å; ε = 0.11863 kcal/mol

Oh σ=3.09289 Å; ε = 0.11703 kcal/mol

H σ=1.40422 Å; ε = 0.00001 kcal/mol

Bond coefficient

H-Oh: K_b=524.34 kcal/mol $Å^2$

r_0= 0.96 Å

P-OI: K_b=254 kcal/mol Å^2

r_0= 1.53 Å

Angle Coefficient

OI-P-OI: K_θ=125 kcal/mol rad^2

θ_0= 109.50^0

SI2.2) Minimization, Equilibration and Deformation

— Molecular dynamic simulation consists of 3 important steps. 1) Energy Minimization, 2) Equilibration and 3) Production (deformation in this study). During energy minimization the particle coordinates are so adjusted as to occupy a lower energy state. Particle velocities are not supplied or modified in this stage. Thus only the potential energy is minimized while the kinetic energy remains 0. A typical energy plot obtained in our simulations during minimization is shown in Figure.

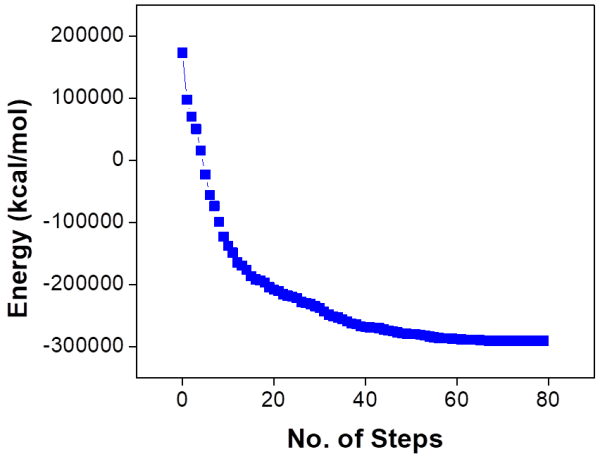

Figure S2.2.1: Energy Minimization

— During equilibration particles are assigned velocities and they evolve in NPT dynamics to attain the required temperature and pressure. The equilibration of temperature and pressure over the last 100 ps before deformation is shown in Figure.

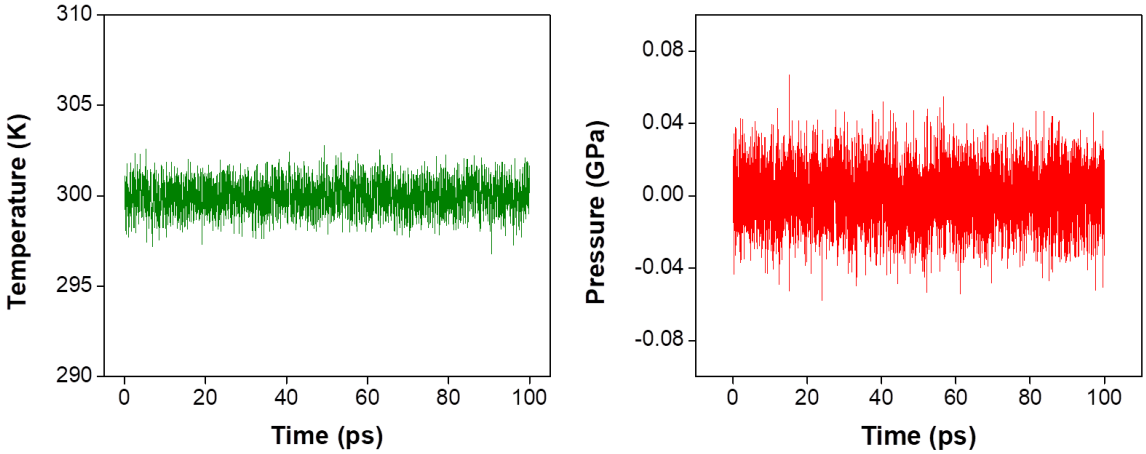

Figure S2.2.2: Equilibration of Temperature and Pressure

— Once the system is equilibrated, the simulation box is deformed at a rate of 0.0002L/fs where L is the size of the box in Z direction. The pressure in X and Y direction are maintained at 0. The pressure (Pz) in Z direction is determined and the stress is estimated as (-Pz).

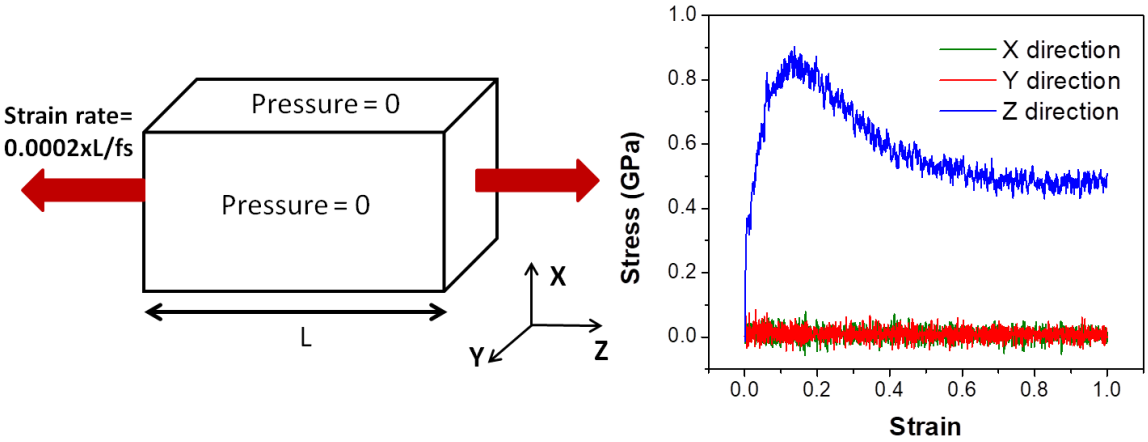

Figure S2.2.3: Deformation and variation of pressure in X, Y, Z direction

— Snapshots from equilibration and deformation stages in the simulation are provided in Figure.

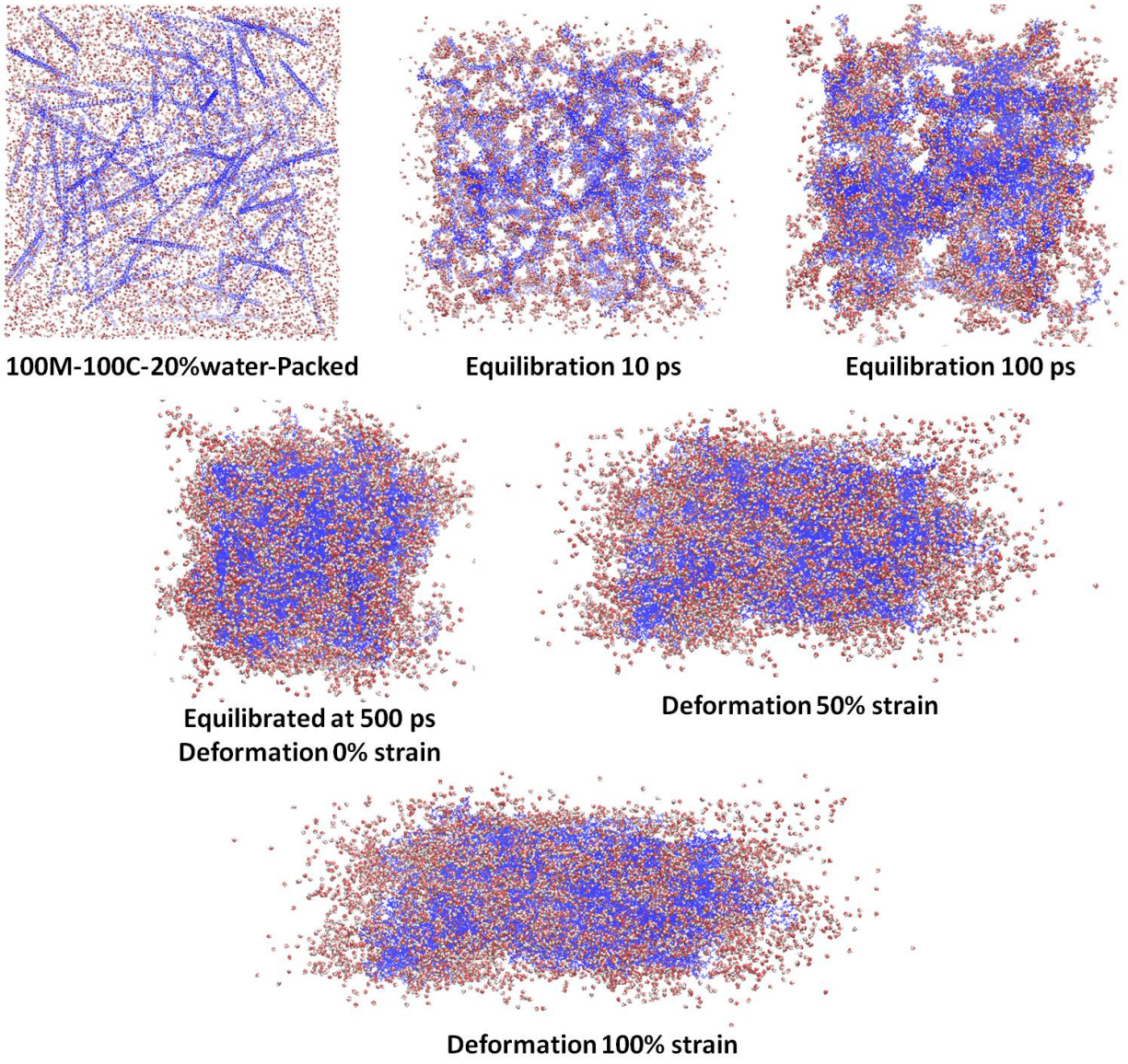

Figure S2.2.4: Snapshots of the model at different stages of MD Simulation

SI3) Variation of Hardness and Loss Modulus values for PLA and PLA/5HAP nanocomposite over a period of 0-55 days.

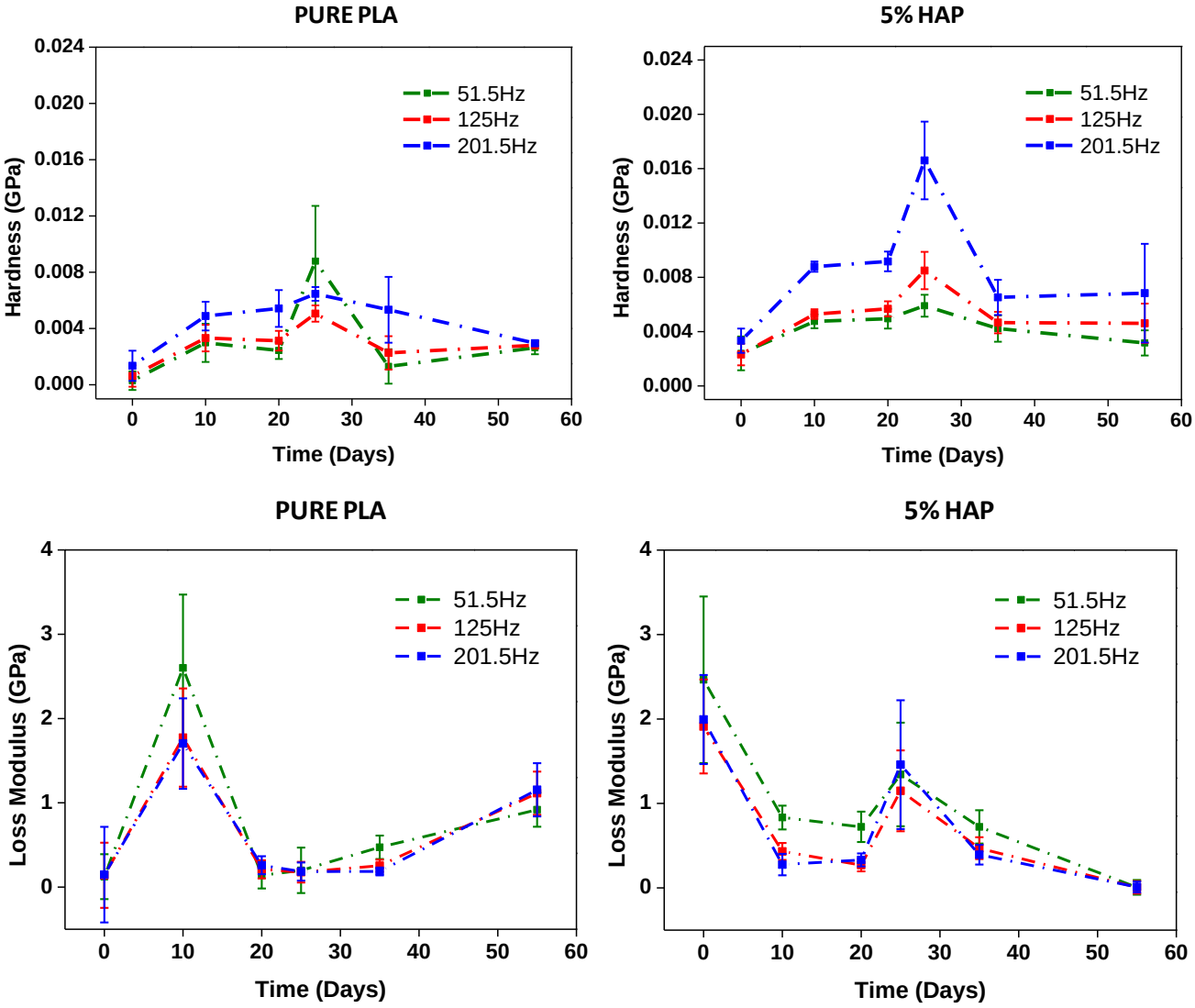

Figure S3: Variation of hardness and loss modulus with respect to time

SI4) Frequency sweep data of storage modulus for pure PLA and 1%, 5% and 10% HAp-PLA nanocomposite over a period of 0 to 55 days

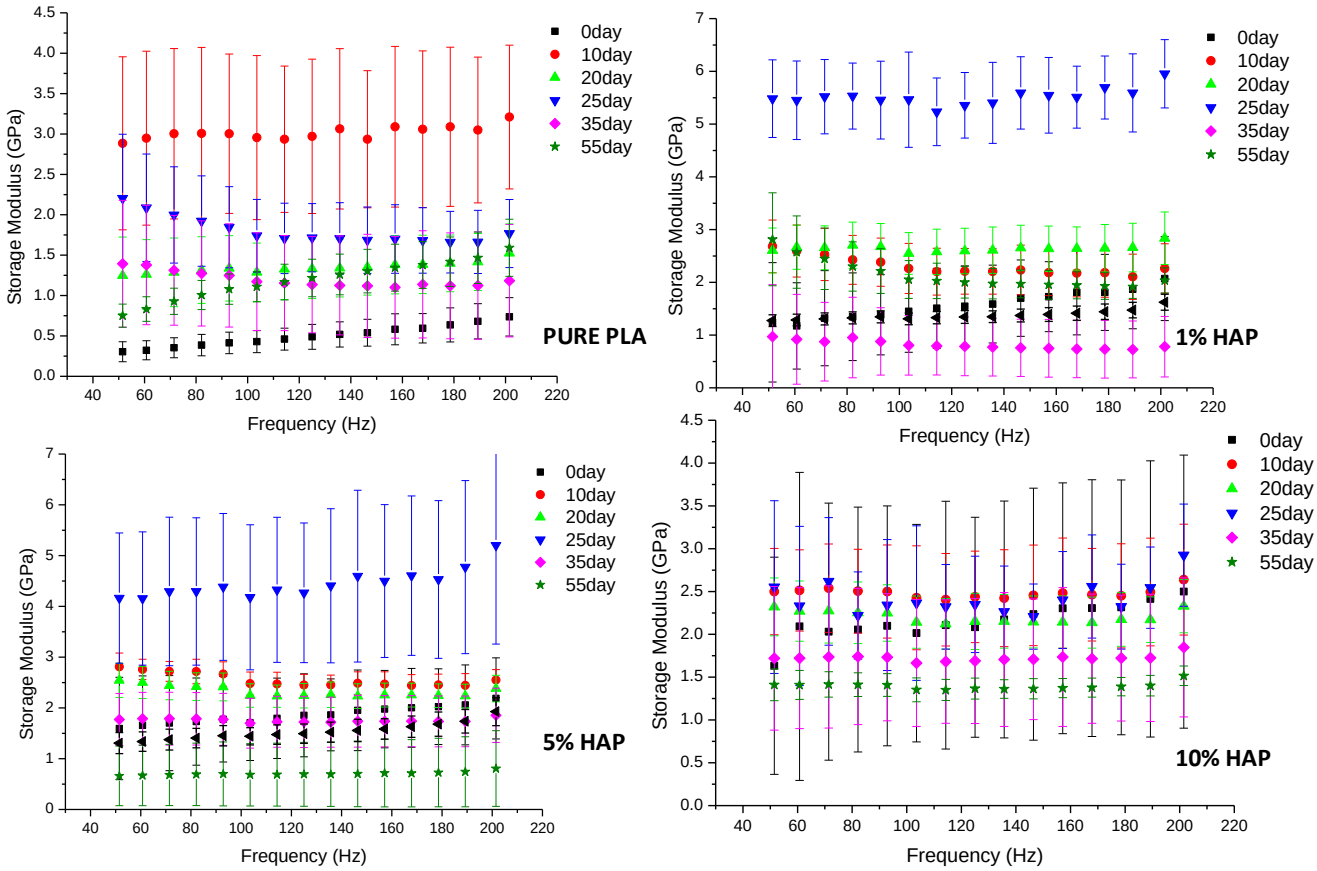

Figure S4: Frequency sweep data for PLA, PLA/1%HAp, PLA/5% HAp, PLA/10%HAp over a period of 0-55 days

SI5) Summary of molecular dynamic simulations and estimation of Young's modulus from the stress strain plot

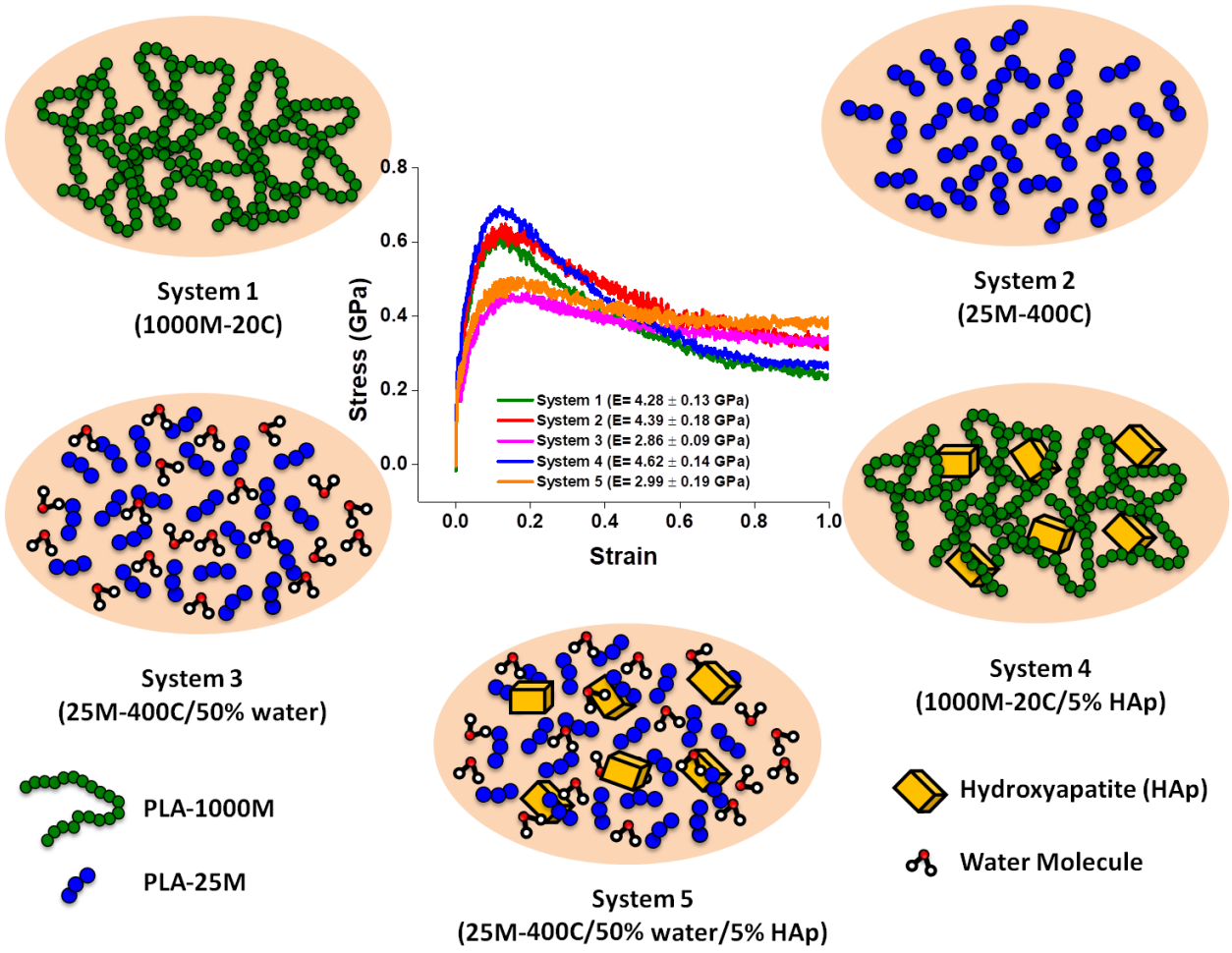

Figure S5: Stress strain plot for various systems (System 1-5) with varying degree of polymerization, water content and %HAp

SI6) Additional Simulations Performed

1) Varying degree of polymerization with same percentage of water

In this set, the water content is maintained ay 5% (low) for different polymerization degree (200M-50C, 100M-100C, 50M-200C and 25M-400C). It is observed that there is an increase in the Young's Modulus (E) obtained from the slope of the stress-strain plot. This increase can be attributed to the formation of short water bridges between the polymer chains. These shorter bridges aid the load transfer. They also compact the entangled polymer chains by filling the free volumes in between the chains and forming physical cross-links between the polymer chains. These factors combined result in an increase in mechanical properties at lower water content.

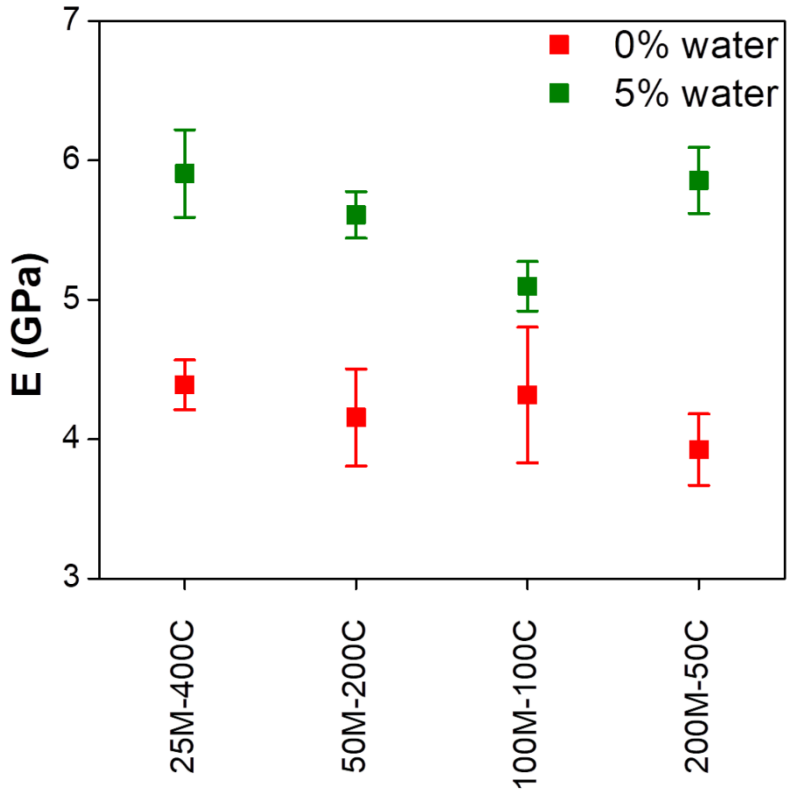

Figure S6.1: Comparison between the storage modulus of PLA systems with varying degrees of polymerization a) without water (0%) and b) with 5% water.

2) Same degree of polymerization with varying percentage of water

In the second set, we varied the water content from 5% to 20% for the same polymerization degree (100M-100C). It was observed that the Young's modulus rises initially for 5% water content but subsequently reduces as the water content increases. This can be attributed to the fact that as you increase the water content, longer water bridges form which are more susceptible to failure under tension and shear.

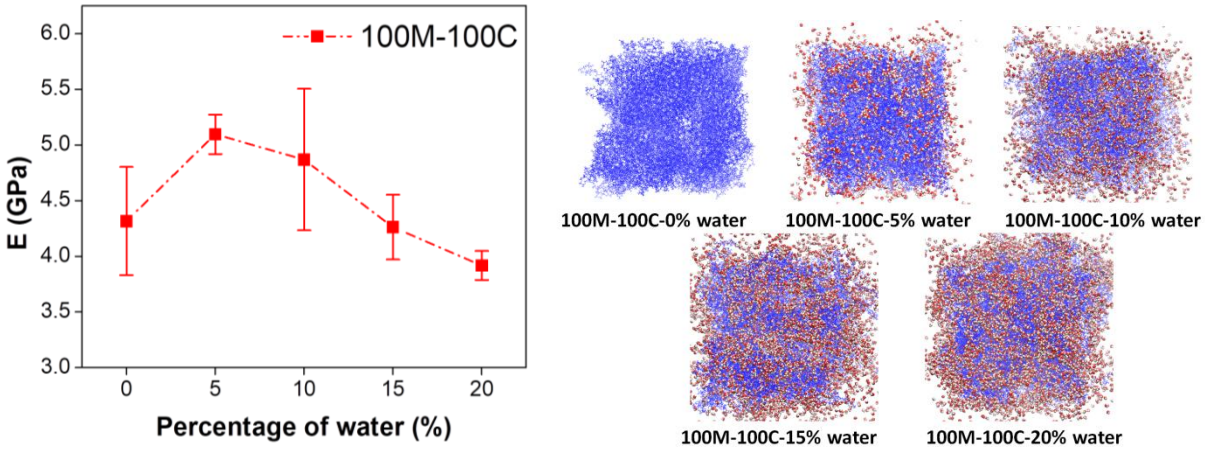

Figure S6.2: Comparison between the storage modulus of PLA systems with same degree of polymerization with varying water saturation (0% to 20%)