Electronic Supplementary Material (ESI) for Journal of Materials Chemistry B.

Supplementary Information

Clustering of Hydroxyapatite on Super-Twisted Collagen Microfibril under Mechanical Tension

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Supplementary Table S1. Force field parameters of HAP.

Atom	**Charge**[1]	**Non-bonded van der Waals parameters**[2, 3]
Ca	+2.0	ε = 0.496 kJ/mol, σ = 0.294 nm
P	+2.6	ε = 2.447 kJ/mol, σ = 0.349 nm
O(P)	-1.4	ε = 1.054 kJ/mol, σ = 0.303 nm
O(H)	-1.6	ε = 0.490 kJ/mol, σ = 0.309 nm
H	+0.6	ε = 0.192 kJ/mol, σ = 0.140 nm
Bond type		**Bond parameters**[2, 4]
P-O stretch		r_0 = 0.157 nm, k_b = 359824 kJ/mol/nm^2
O-P-O bend		θ_0 = 109.5°, k_θ = 1046 kJ/mol/rad^2
O-H stretch		r_0 = 0.096 nm, k_b = 438767 kJ/mol/nm^2

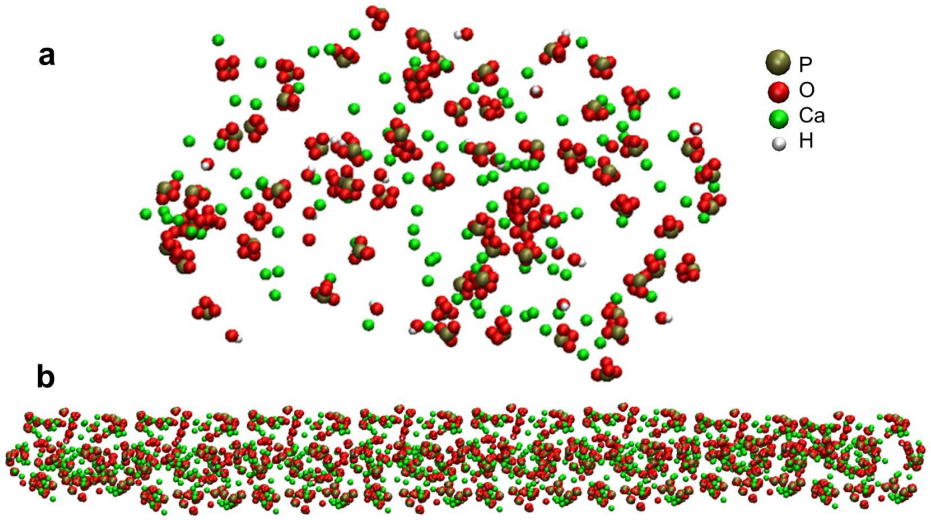
In Table S1, ε is the depth of the potential well of Lennard-Jones potential, and σ is the distance at which the van der Waals potential is zero.

Lennard-Jones potential: $V_{LJ} = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$

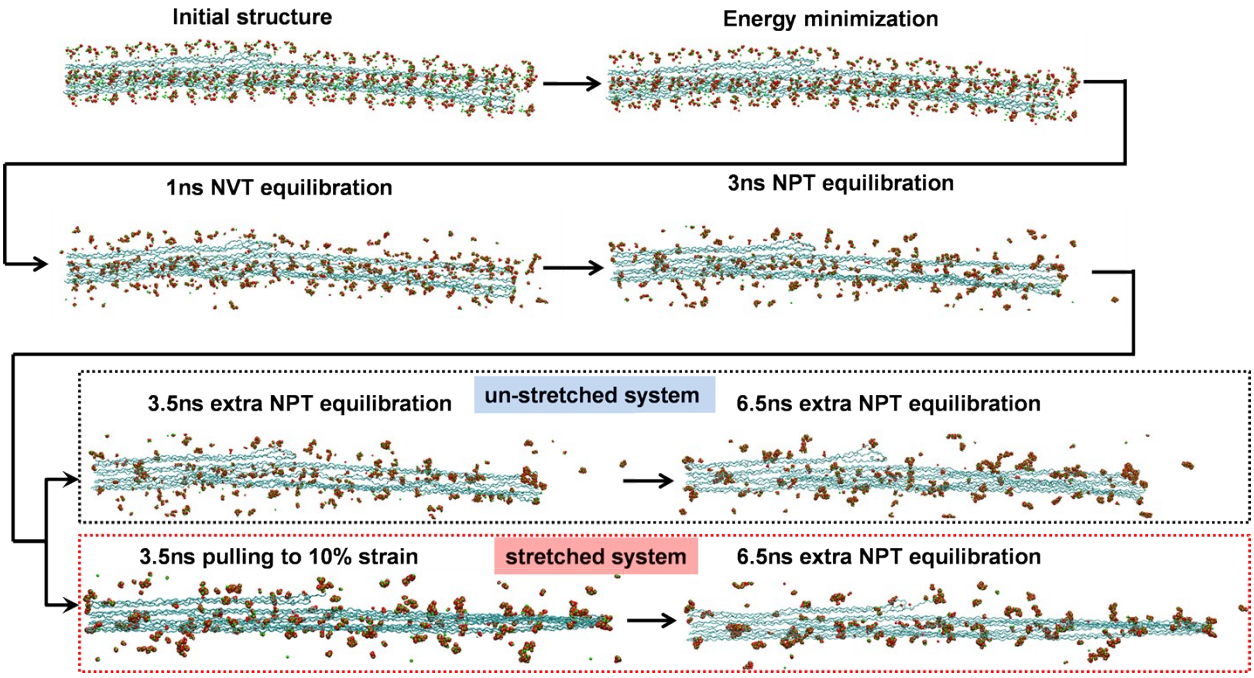
r_0 is the equilibrium bond length for covalent bond stretching, and k_b is the force constant.

θ_0 is the equilibrium bond angle for covalent bond angle bending, and k_θ is the force constant.

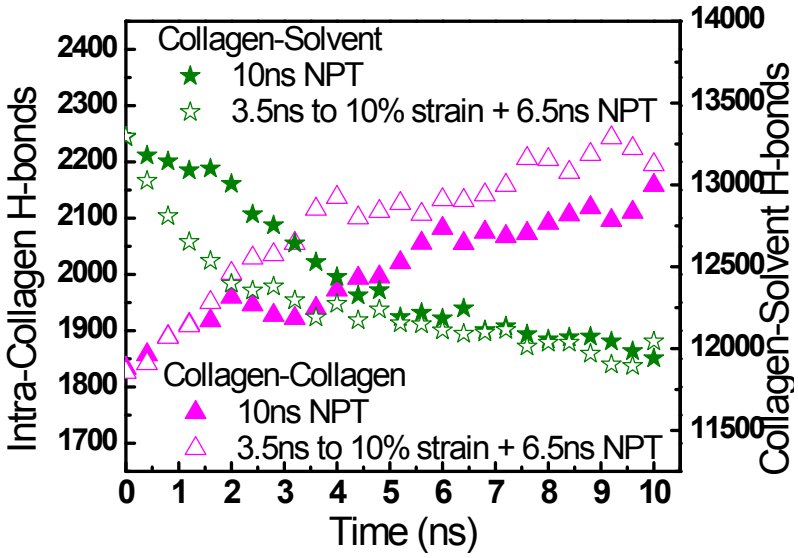
Refer to GROMACS[5] and its manual for the formulations of the potential functions.



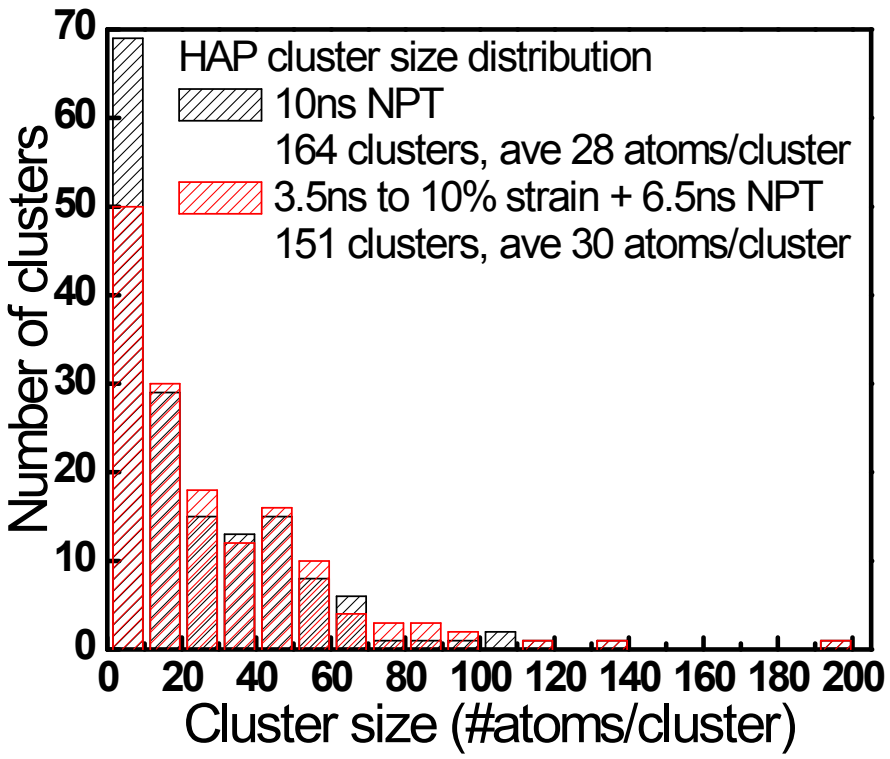
Supplementary Figure S1. *Discrete HAP ion systems for building collagen microfibril-HAP composite.* ***(a)*** *Equivalent to 12 unit cells of HAP.* ***(b)*** *Equivalent to 96 unit cells of HAP, in the final model of collagen microfibril-HAP composite.*



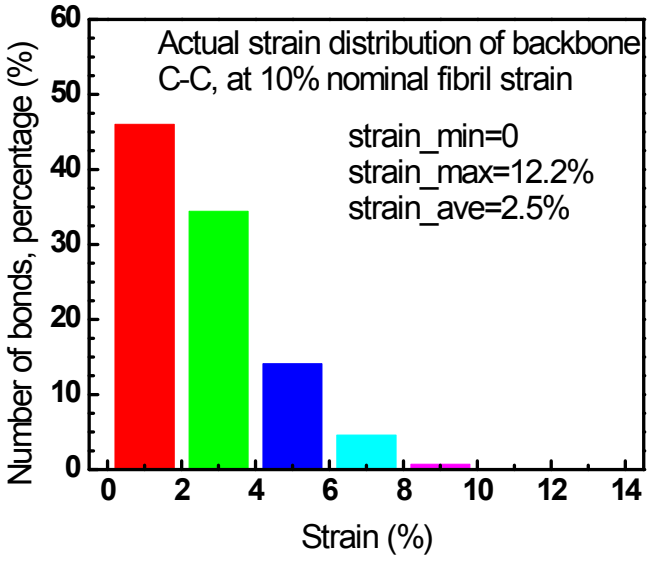
Supplementary Figure S2. *Flow chart of simulation stages, with atomic configuration at the end of each stage.*



Supplementary Figure S3. *Comparison of number of hydrogen bonds within collagen and between collagen and water, for two systems at the same simulation time (one un-stretched configuration during 10 ns extra equilibration, and one configuration stretched for 3.5 ns to 10% followed by 6.5 ns extra equilibration).*



Supplementary Figure S4. *Histograms of the HAP cluster size distribution of the two configurations (after 10 ns extra NPT vs after 3.5 ns stretching to 10% plus 6.5 ns extra NPT). The abscissa is the cluster size intervals, and the ordinate is the number of clusters in each interval.*



Supplementary Figure S5. *Distribution of actual tensile strain of backbone C-C bonds, at nominal engineering strain of 10% in collagen microfibril. The majority (over 80%) of the C-C bonds experienced a strain less than 4%, and only 3 out of 3013 C-C bonds had a strain larger than 10%.*

Supplementary Movies. 2 movies are available in the SI. These movies show the following:

Movie S1. Uniaxial tension of a D-period collagen microfibril and HAP cluster formation, followed by extra equilibration. For collagen microfibril, the final strain is 10% at 3.5 ns, and the pulling rate is 0.002 nm/ps. During 6.5 ns extra equilibration, collagen microfibril is kept at 10% strain by only fixing the N- and C- termini. Collagen chains are in cyan. In HAP minerals, Ca is in Green, P in Gold, O in Red, and H in White.

Movie S2. 10 ns extra equilibration of a D-period collagen microfibril and HAP model, without mechanical stretching. Collagen chains are in cyan. In HAP minerals, Ca is in Green, P in Gold, O in Red, and H in White.

Supplementary References

References

1. S. Hauptmann, H. Dufner, J. Brickmann, S. M. Kast and R. S. Berry, *Physical Chemistry Chemical Physics*, 2003, **5**, 635-639.
2. R. Bhowmik, K. S. Katti and D. Katti, *Polymer*, 2007, **48**, 664-674.
3. R. B. Best, X. Zhu, J. Shim, P. E. M. Lopes, J. Mittal, M. Feig and A. D. MacKerell, *Journal of Chemical Theory and Computation*, 2012, **8**, 3257-3273.
4. T.-J. Lin, *PhD dissertation, Department of Polymer Engineering,The University of Akron*, 2013.
5. H. J. C. Berendsen, D. van der Spoel and R. van Drunen, *Computer Physics Communications*, 1995, **91**, 43-56.