Yield and Failure Behavior Investigated for Cross-Linked Phenolic Resins Using Molecular Dynamics

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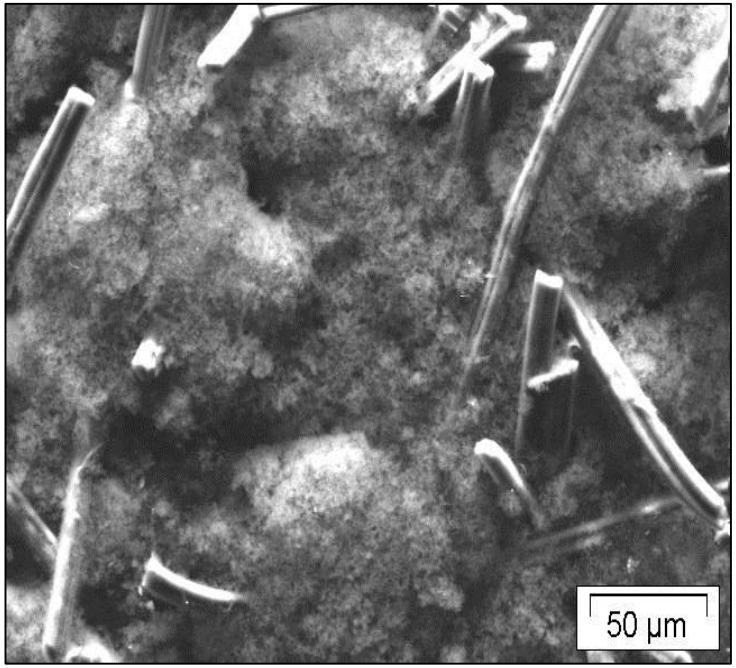
AIChE 2016

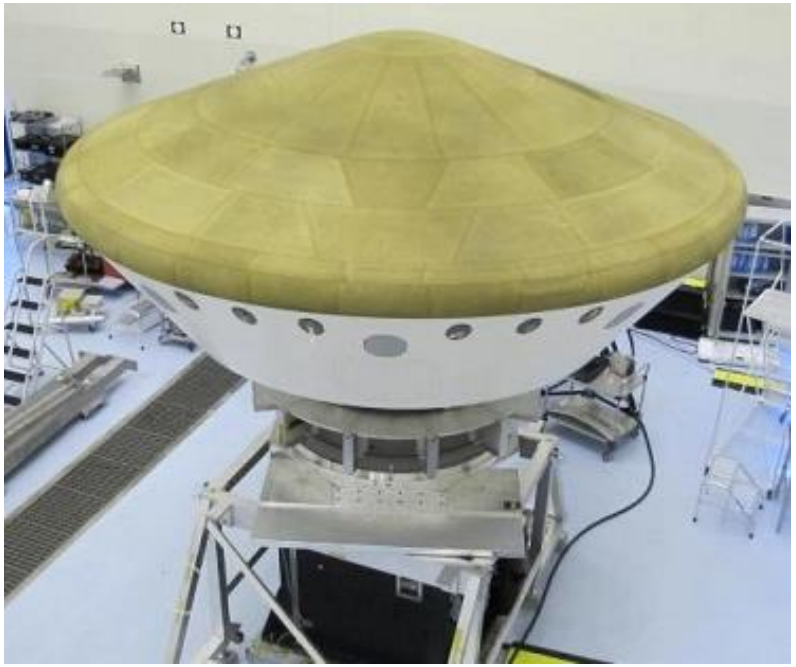
Session: **Atomistic and Molecular Modeling and Simulation of Polymers**
Date: **Monday, November 14, 2016**
Session Time: 3:15 PM - 5:45 PM

Motivation

PICA: Carbon Fiber/Phenolic Matrix[+]



Design Variable: Polymer Resin



MSL (Mars Science Laboratory)
Image credit NASA/JPL. CalTech

[+]Stackpoole M. Sepka S., Cozmuta I. 46th AIAA Aerospace Sci. Meeting and exhibit. (Jan. 2008)

Molecular Dynamics Simulations

Single phenol ring: C_6H_6O

- Linker: Methylene

Chain Length: Linear 9-ring

Force Field:

- OPLS/AA & AMBER (Jorgensen, Cornell) *
- REAXFF (Chenoweth)+

Cross-linking algorithm

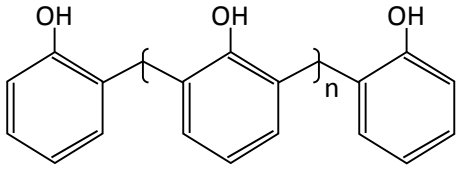
- Bridged individual chains to simulate curing

System:

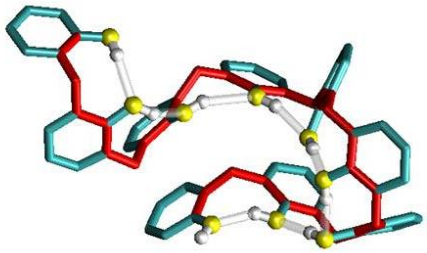
- 67 Å side length
- 216 phenolic chains
- Periodic boundary conditions

Software: LAMMPS

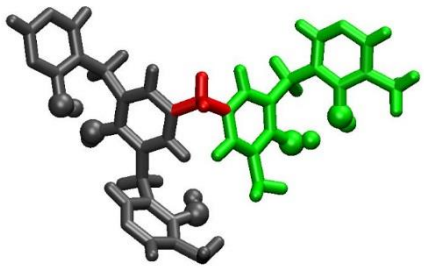
Super Computer: Pleiades at NASA Ames



Ortho-Ortho Phenolic Chain

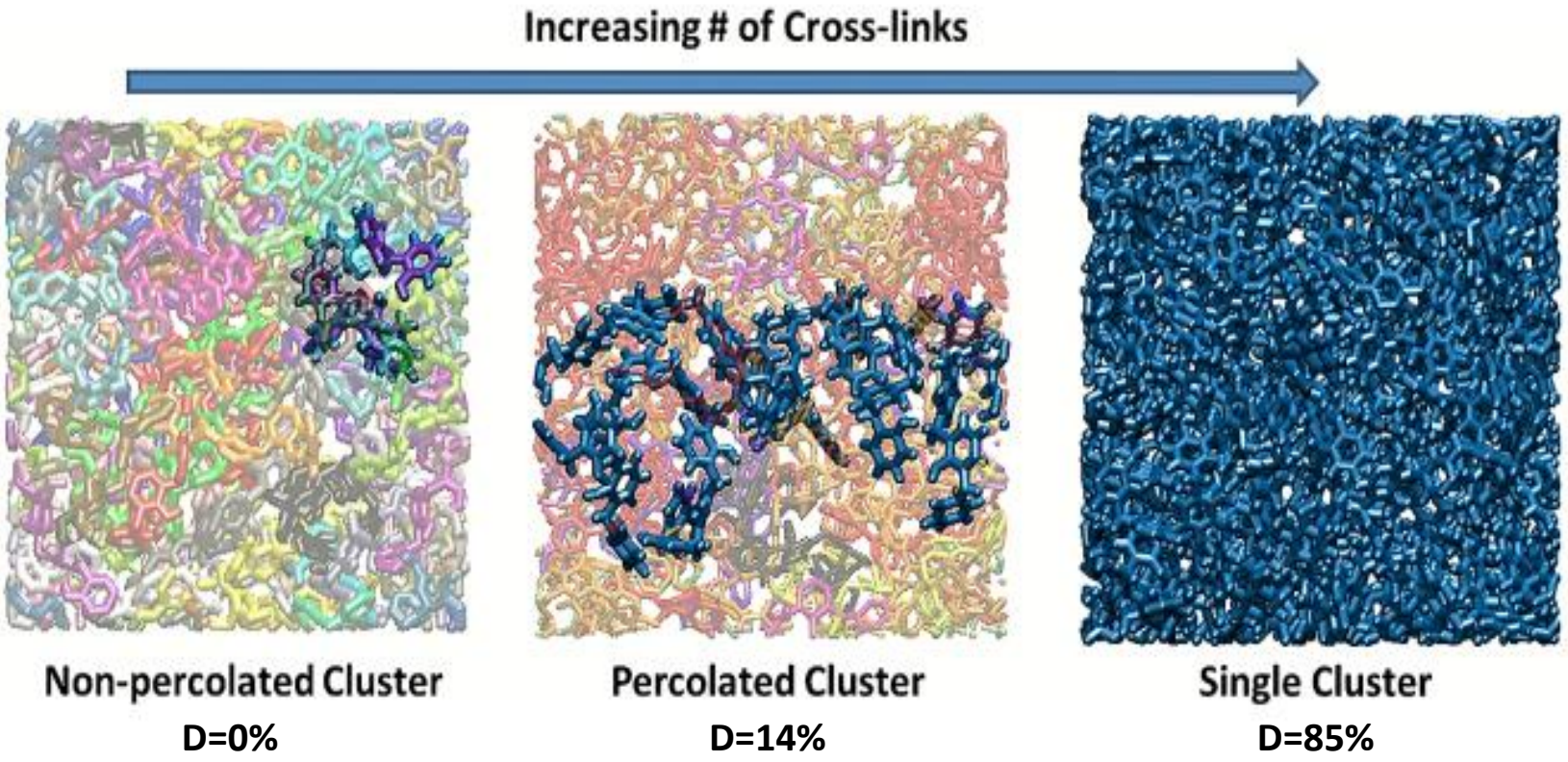


Cross-linked Chains



*Jorgensen, Maxwell, Tirado-Rives JACS (1996), Cornell, Wendy D., et al. *J of the Amer. Chem. Soc.* (1995),
+Chenoweth, Kimberly, Adri CT Van Duin, and W.A. Goddard. *The Journal of Physical Chemistry A* 112.5 (2008).

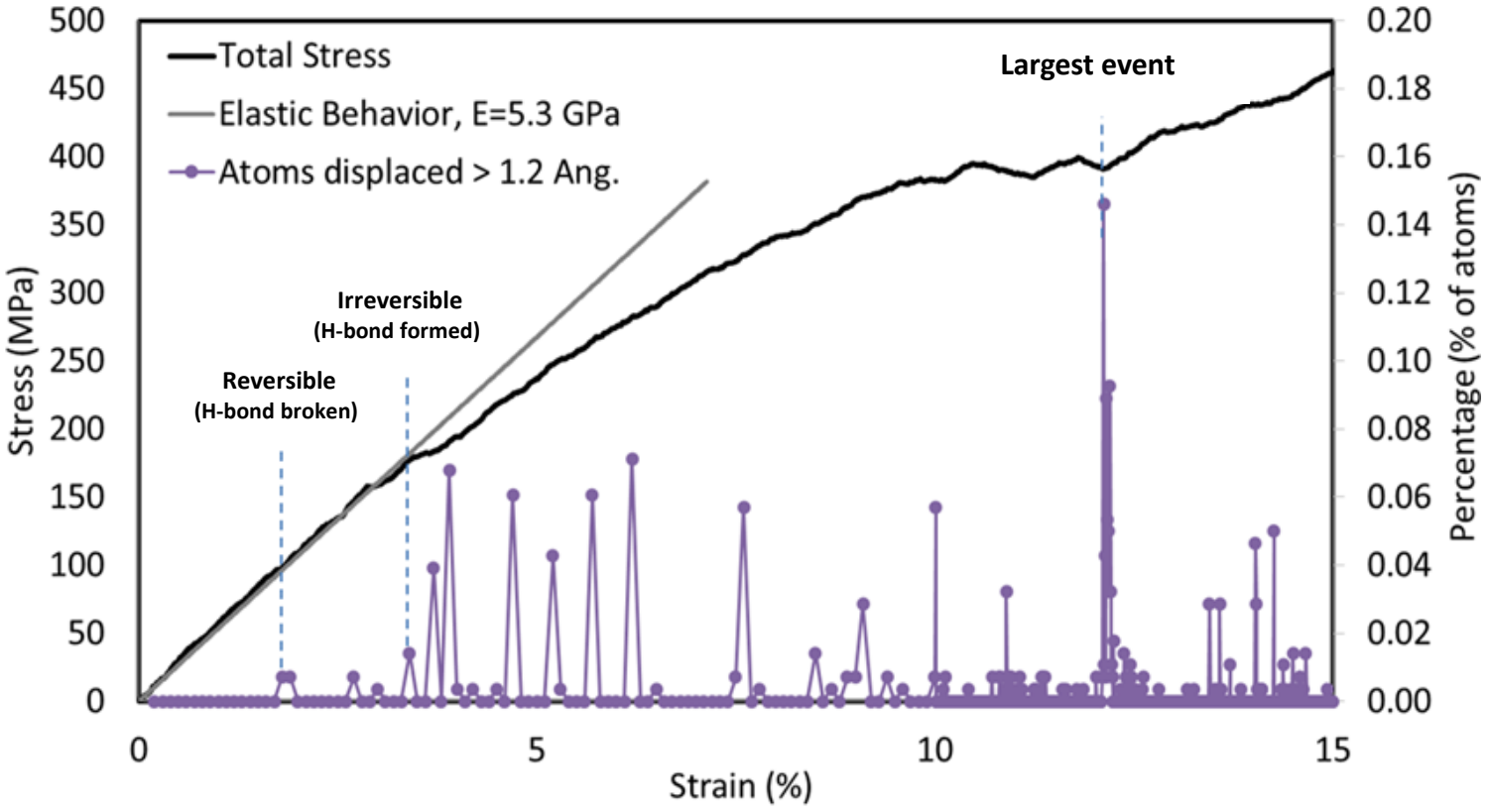
Increasing Degree of Cross-linking



$$D(\%) = \frac{\#\ of\ Bridged\ Aromatic\ Rings}{\#\ of\ Total\ Aromatic\ Rings} * 100\%$$

*Monk, J.D., et al. *Polymer* 62 (2015): 39-49 & Monk, J.D., et al. *Macromolecules* 48.20 (2015): 7670-7680

Low Temperature Stress-Strain Profile

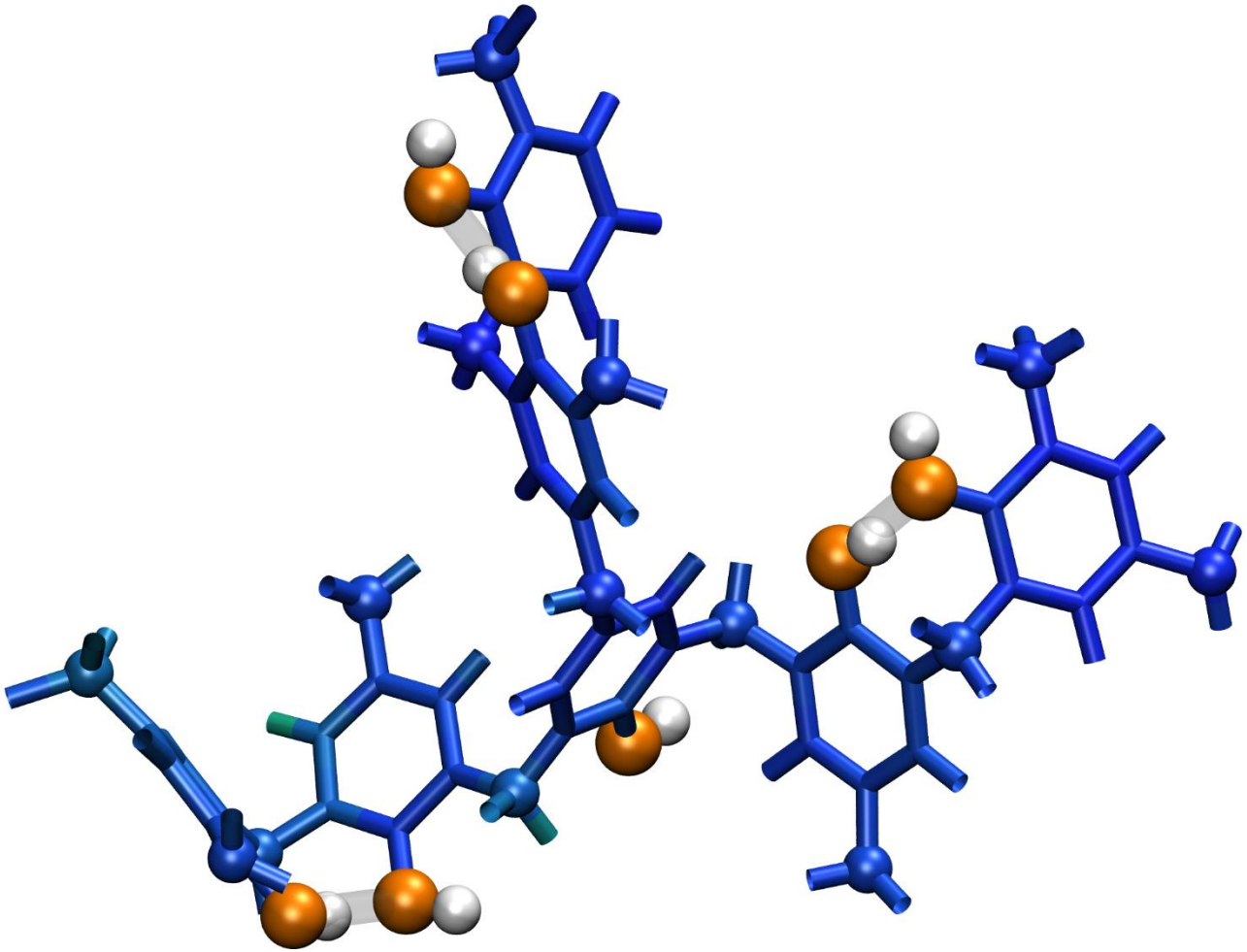


D=85%

T=10K

$\dot{\varepsilon} = 1 \times 10^{8}\ s^{-1}$

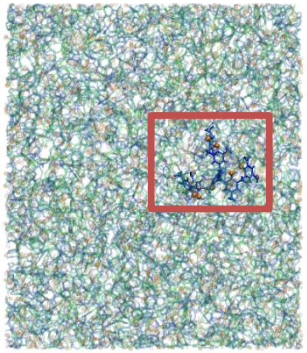
Direction of deformation



High displacement

1.2Å

Low displacement

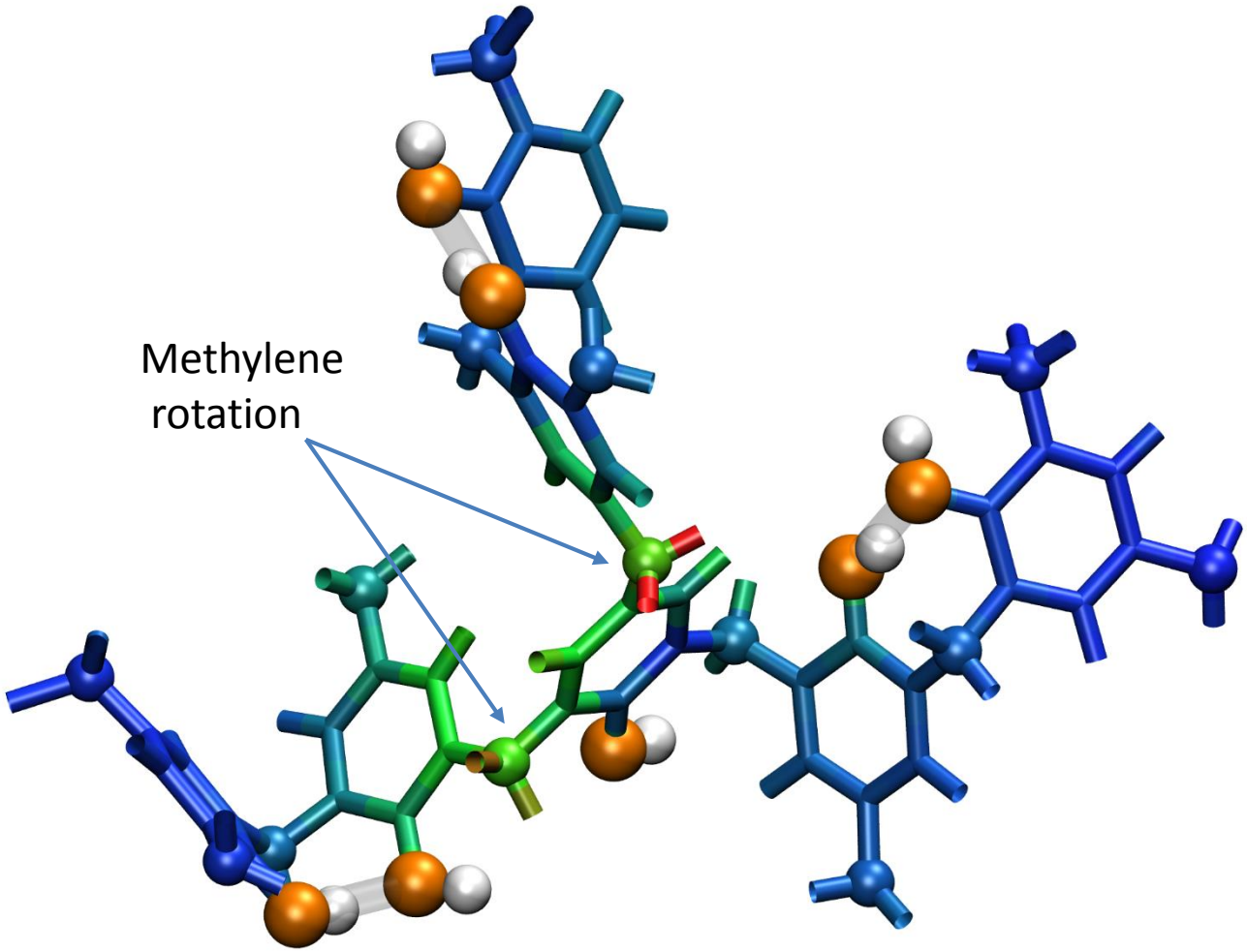


Ɛ =12.09%

Colored by relative radial displacement

Direction of deformation

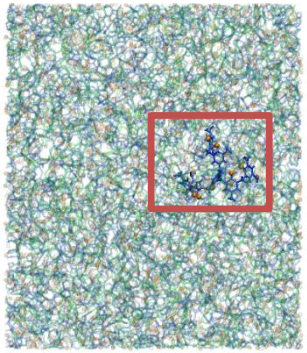
Methylene rotation



High displacement

1.2Å

Low displacement



Ɛ =12.10%

Colored by relative radial displacement

Direction of deformation

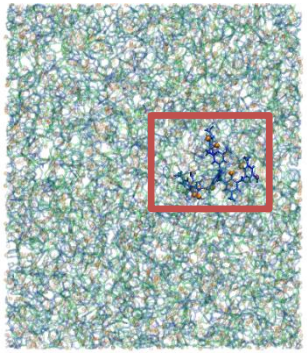
Methylene rotation

H-bond formation

High displacement

1.2Å

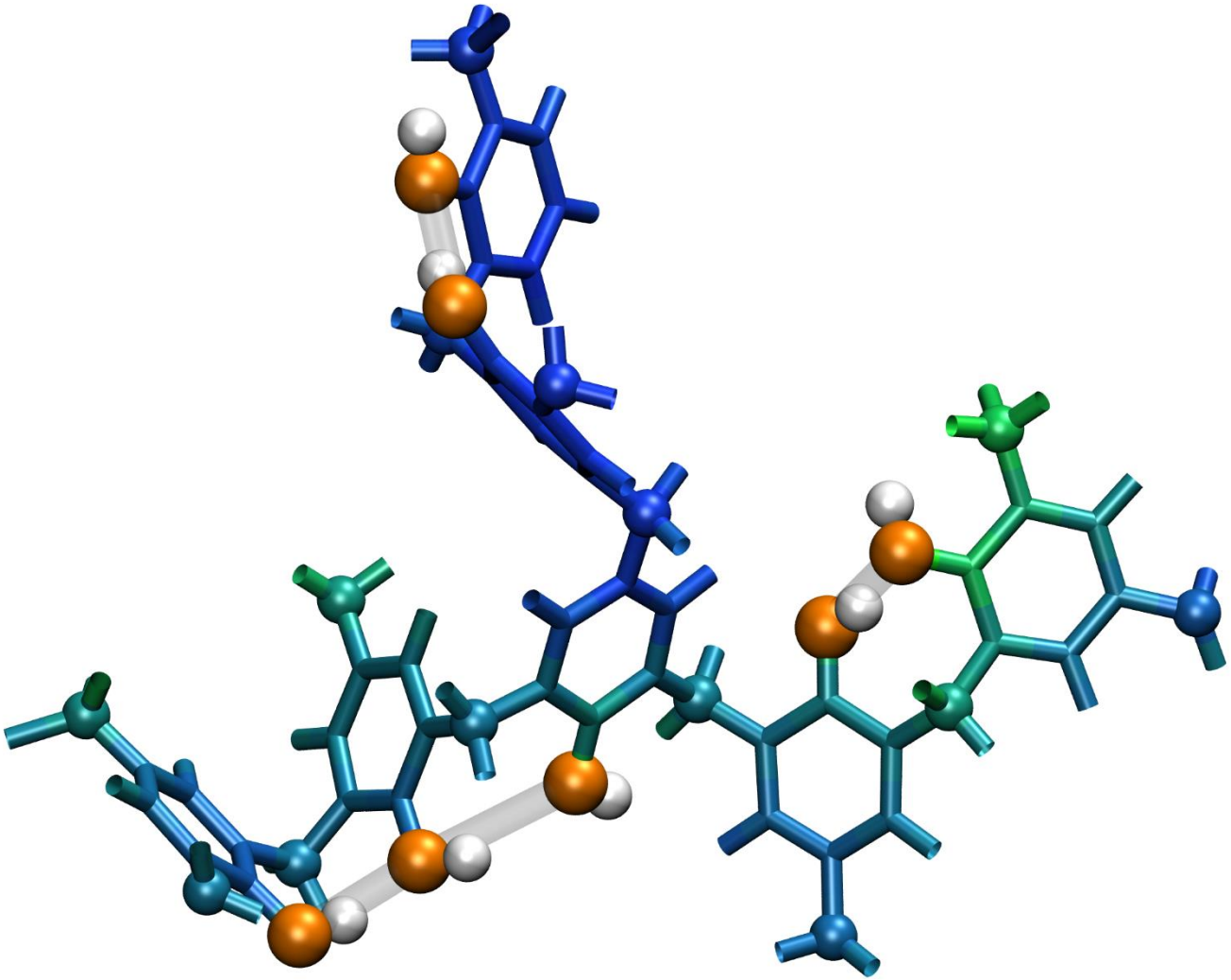
Low displacement



Ɛ =12.11%

Colored by relative radial displacement

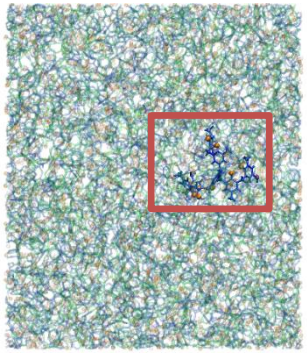
Direction of deformation



High displacement

1.2Å

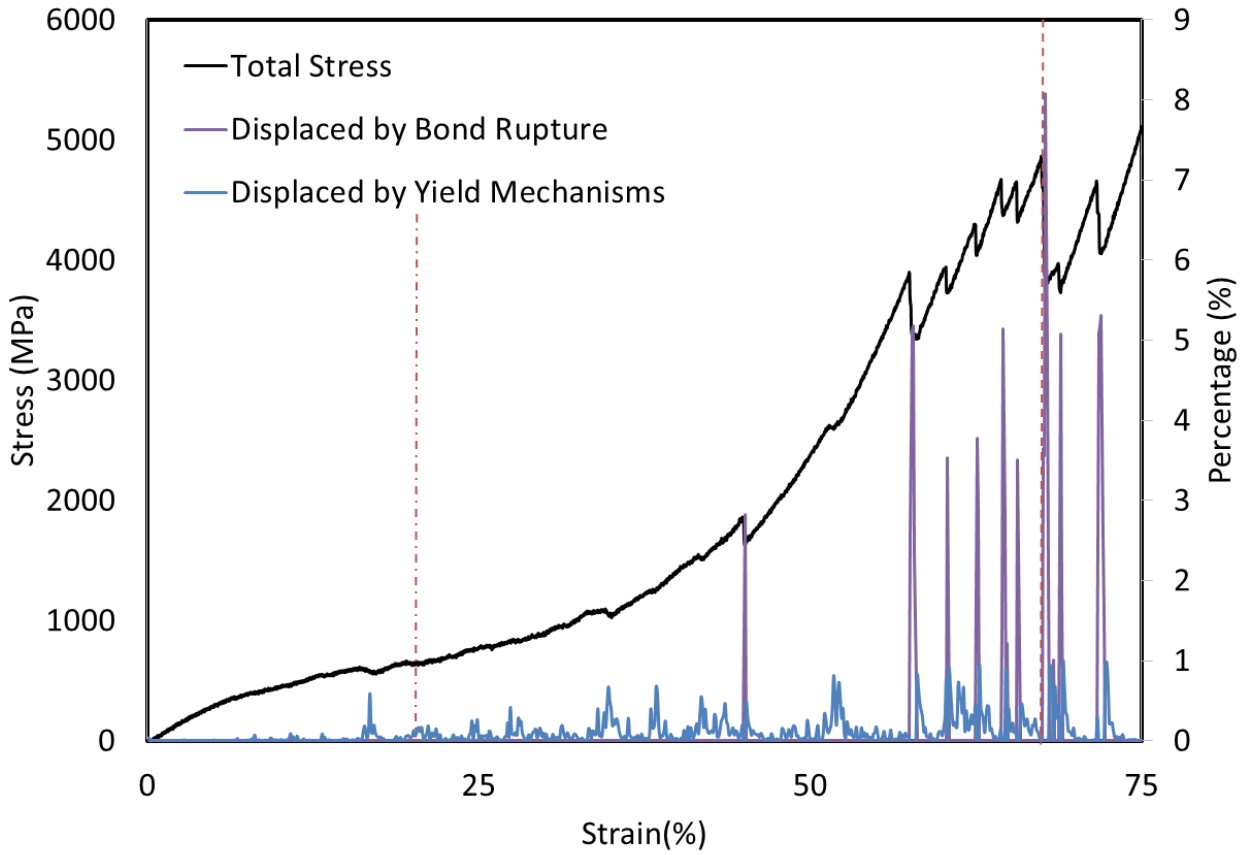
Low displacement



Ɛ =12.12%

Colored by relative radial displacement

Reactive Tensile Simulation

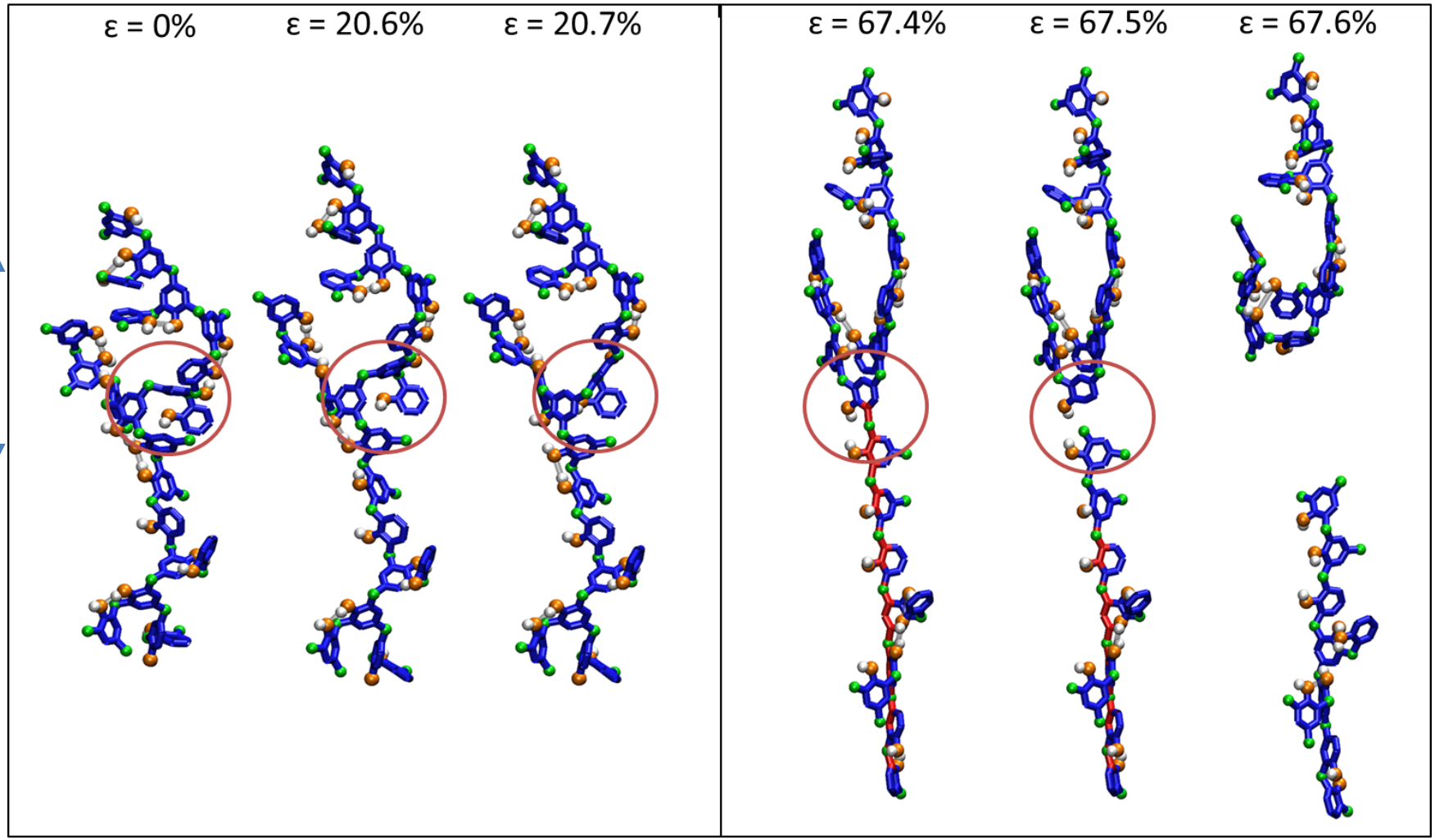


D=85%

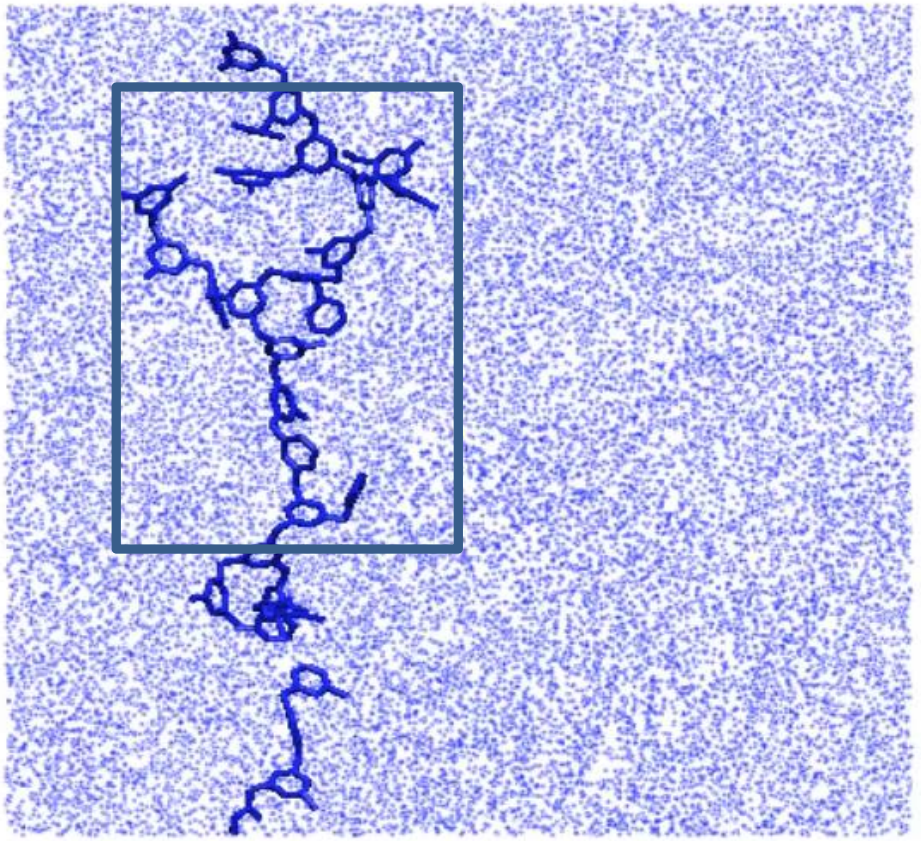
T=10K

$\dot{\varepsilon} = 1 \times 10^{9}\ s^{-1}$

From Yield to Failure

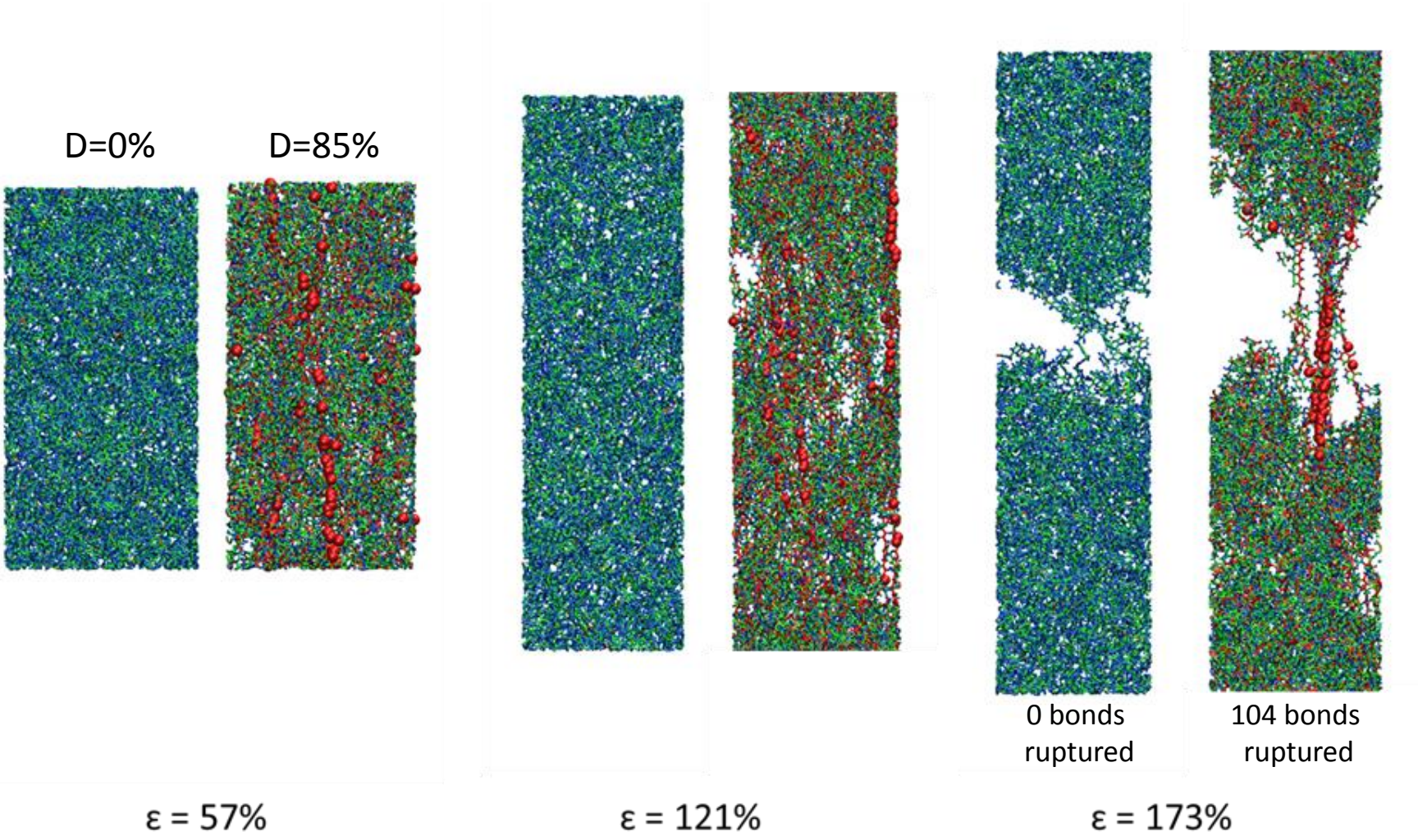


Colored by total atomic stress



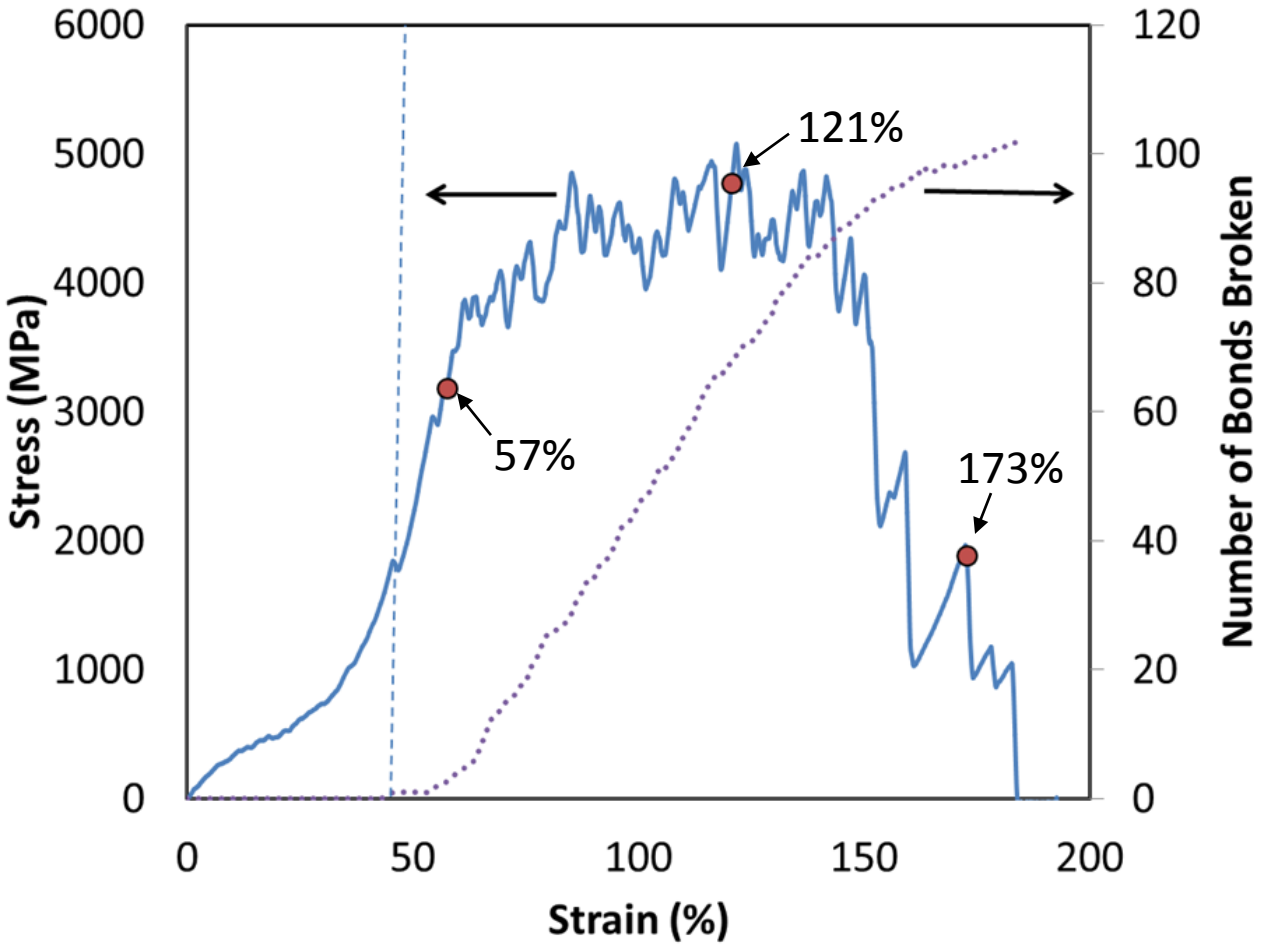
Colored by total atomic stress

Reactive Tensile Simulation To Critical Failure



T=10K

$\dot{\varepsilon} = 1 \times 10^{9}\ s^{-1}$



D=85%

T=10K

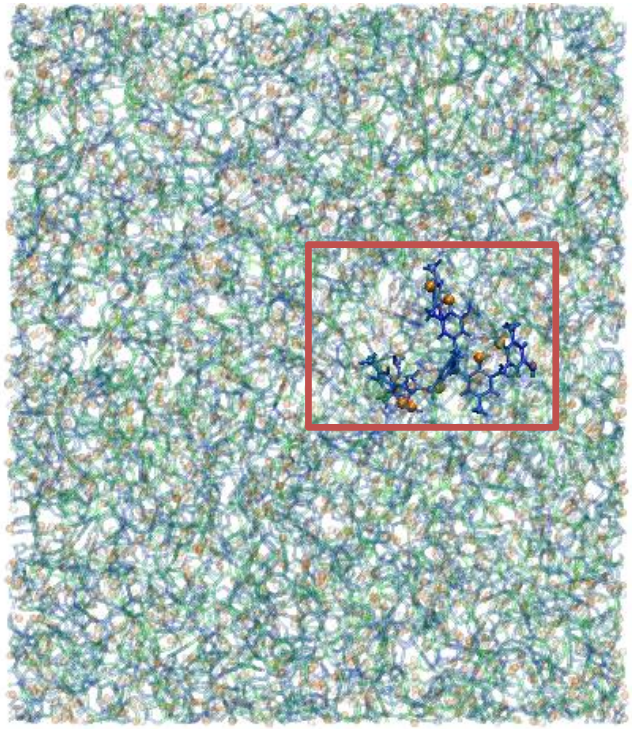
$\dot{\varepsilon} = 1 \times 10^{9}\ s^{-1}$

Conclusion

- Yield events identified as local molecular rearrangements including hydrogen bond formation drive inelastic behavior
- Yield mechanisms assist in stress relief through realignment of carbon backbones.
- Failure along carbon backbones occurs when further realignment is less energetically favorable than bond rupture
- Degree of cross-linking greatly influences the form of failure for glass-like phenolic

Backup Slides

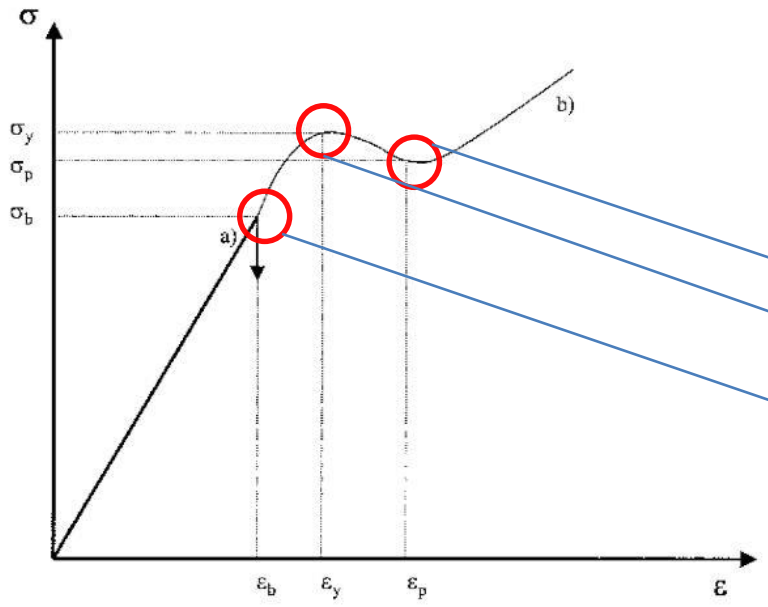
Study of Phenolic Yield Behavior

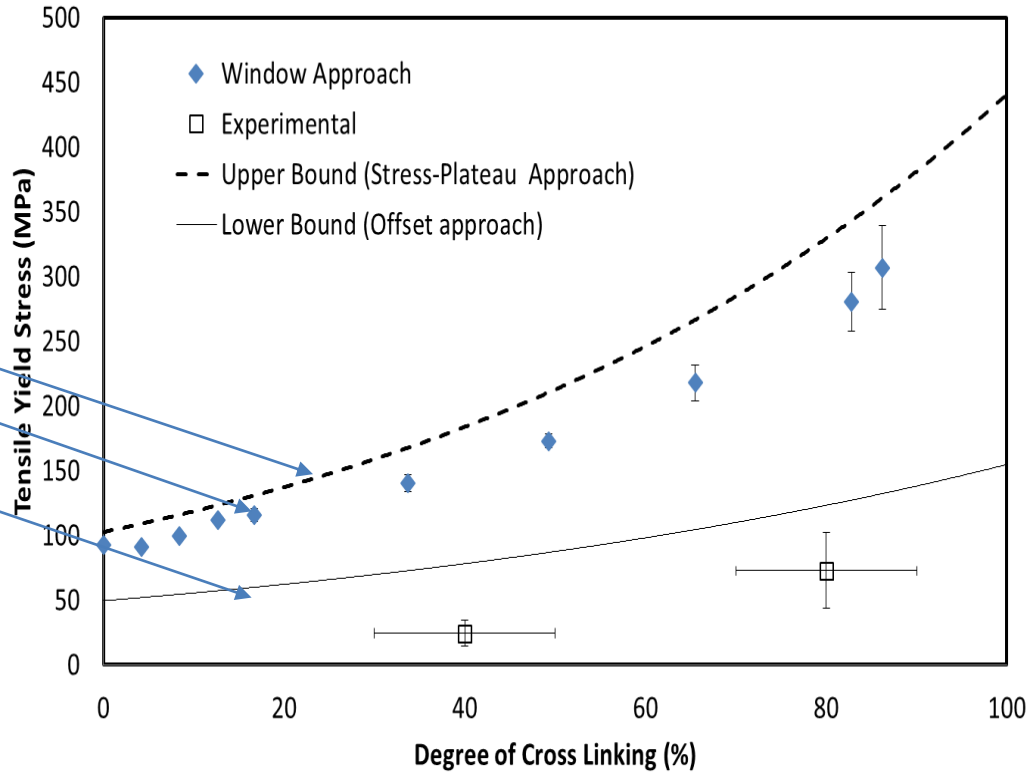


Full scope of study:

- Degree of cross-linking: 0% to 85%
- Strain rates range: 10^{7} to $10^{10.5}$
- Temperature range: 10K to T_g-50K
- Strains: up to 180%
- Tension, compression, and shear deformation simulations

Yield Stress Dependence on Degree of Cross-linking

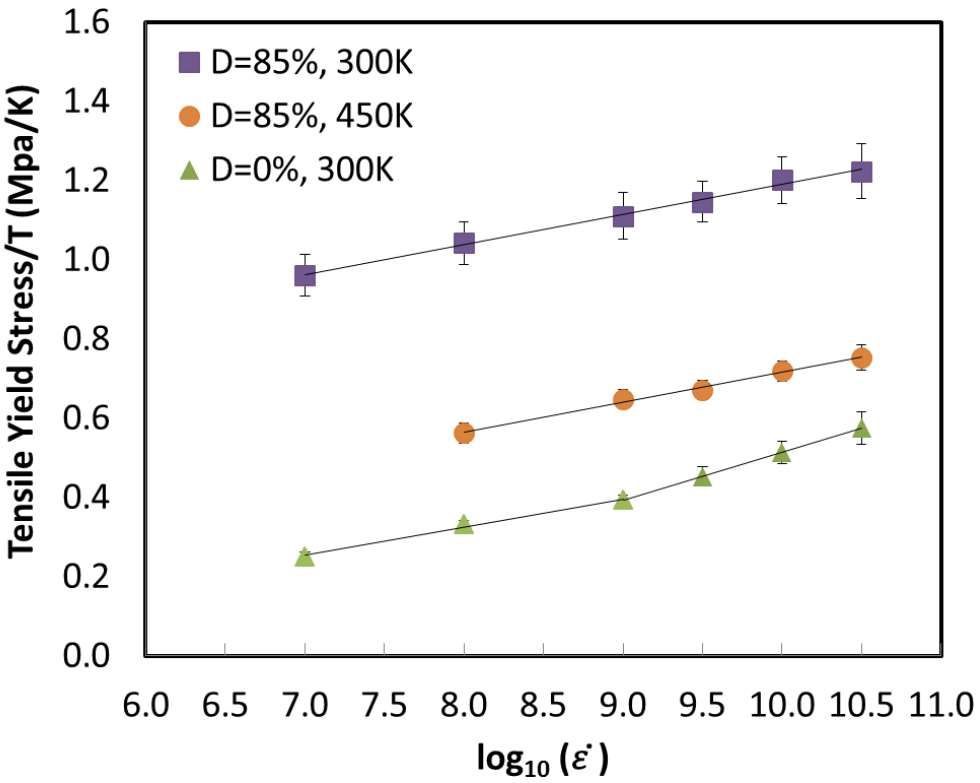




T=300K

$\dot{\varepsilon} = 1 \times 10^{8}\ s^{-1}$

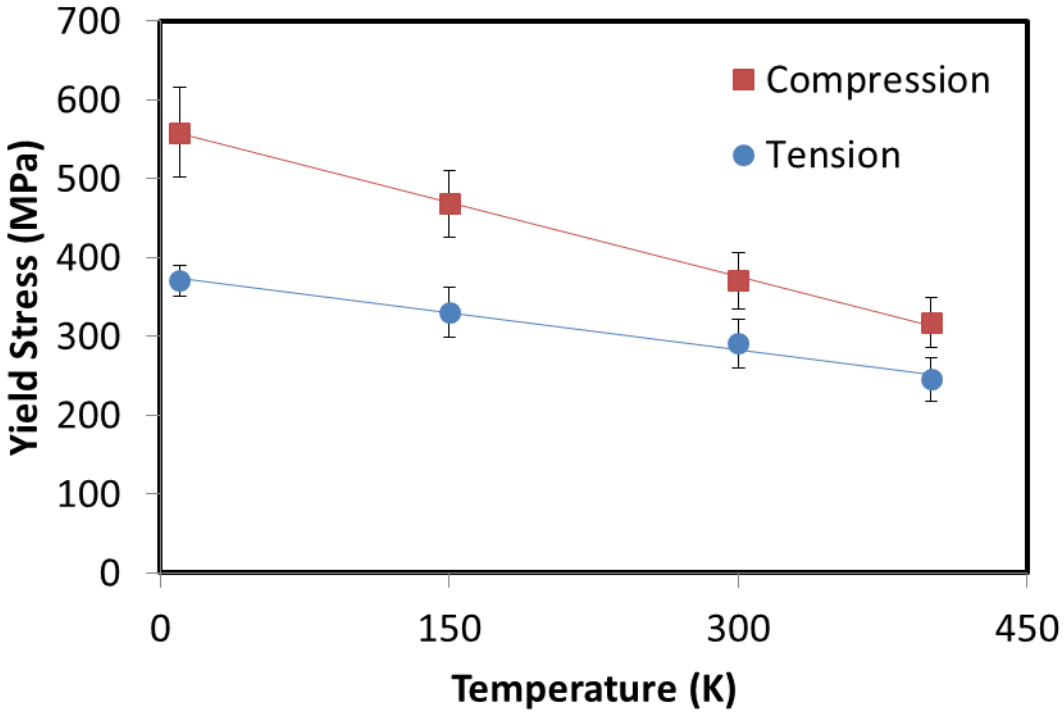
Dependence of Yield Stress on Strain Rate



Activation (v^*) and Transformation (Ω_c) Volumes:

$$v^* = k_b \frac{\ln \dot{\varepsilon}}{\partial \left(\frac{\sigma}{T}\right)} = \Delta \varepsilon^T \Omega_c$$

Dependence of Yield Stress on Temperature (T<Tg)



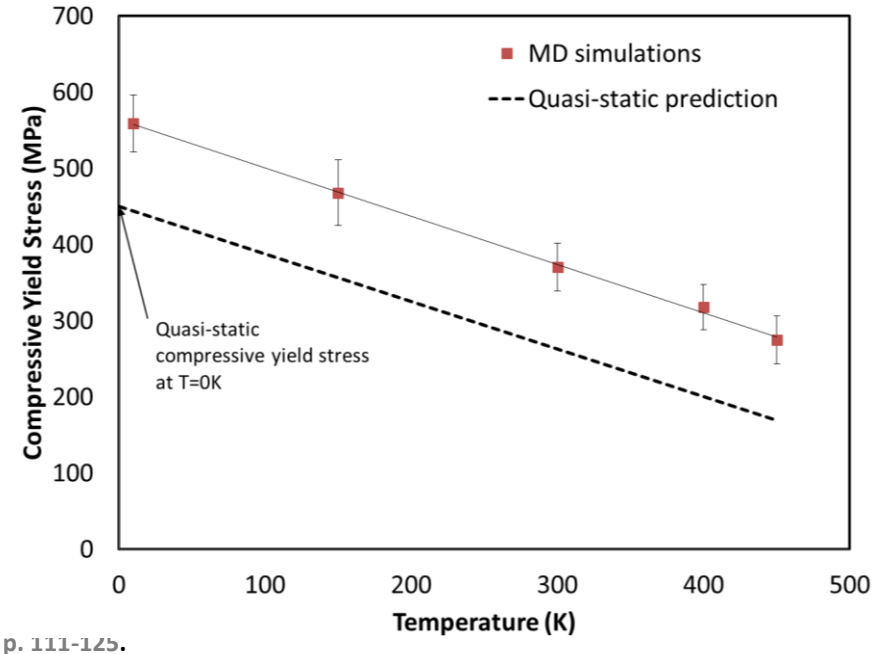
Kambour's relation: $\sigma_y = \sigma_y^* + \beta(T - T^*) for\ T < T_g$

Source of Yield Stress Results	Tension (MPa)	Compression (MPa)	Temperature (K)
MD results, $\dot{\epsilon} = 1 \times 10^8\ s^{-1}$	290 ± 31	370 ± 35	300
Eq. 1, T^* = 300K	384	556	0
Eq. 2, predicted quasi-static	310	450	0
Eq. 3, predicted quasi-static	215	260	300
Experimental	100 ± 5	140 ± 5	300

$$\sigma_y = \sigma_y^* + \beta(T - T^*) for\ T < T_g \quad (1)^*$$

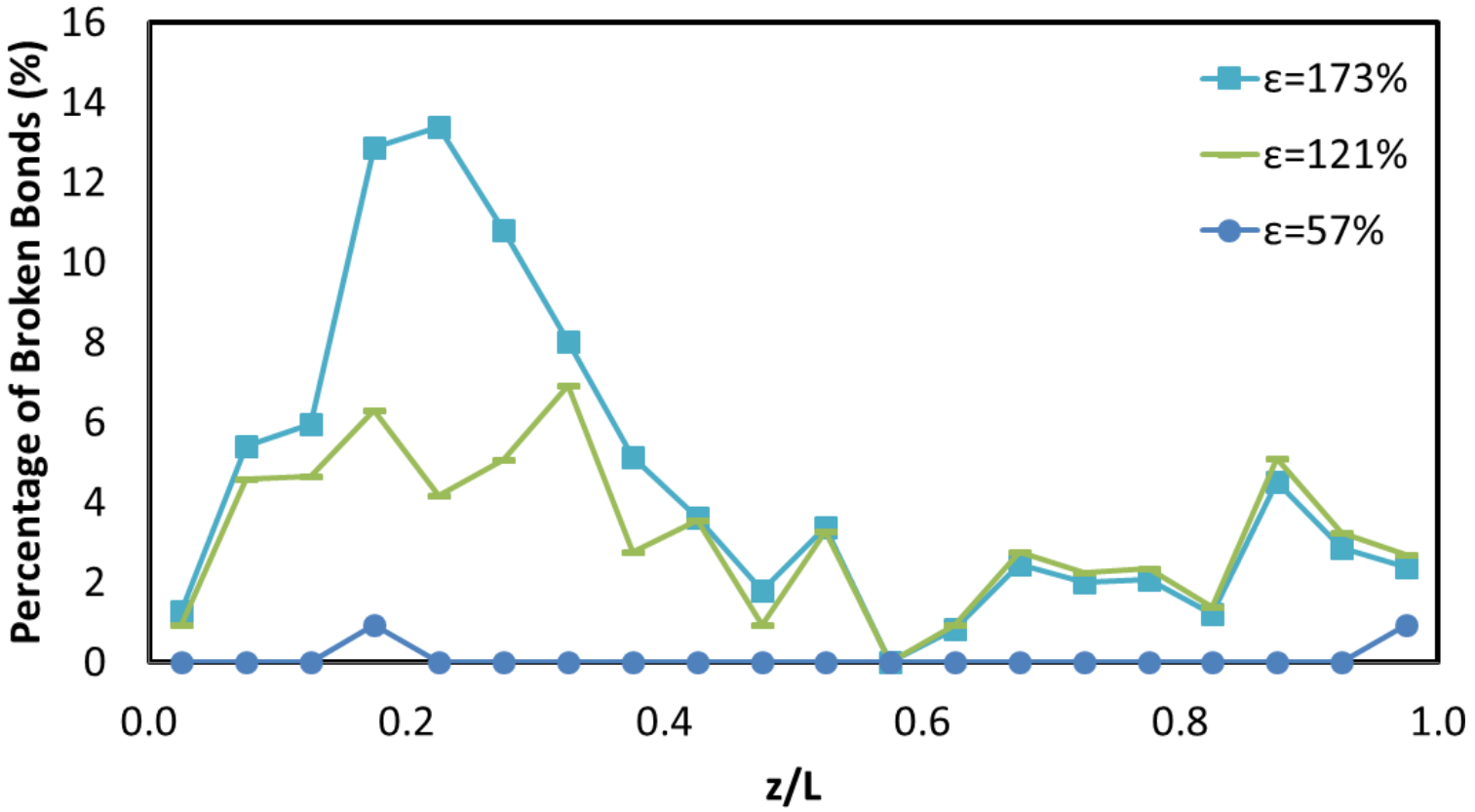
$$\left(\sigma_{Y_c}\right)_{T=0} = \frac{\sqrt{3}}{2}\frac{0.077}{1-\nu^2} E_{T=0} \quad (2)^+$$

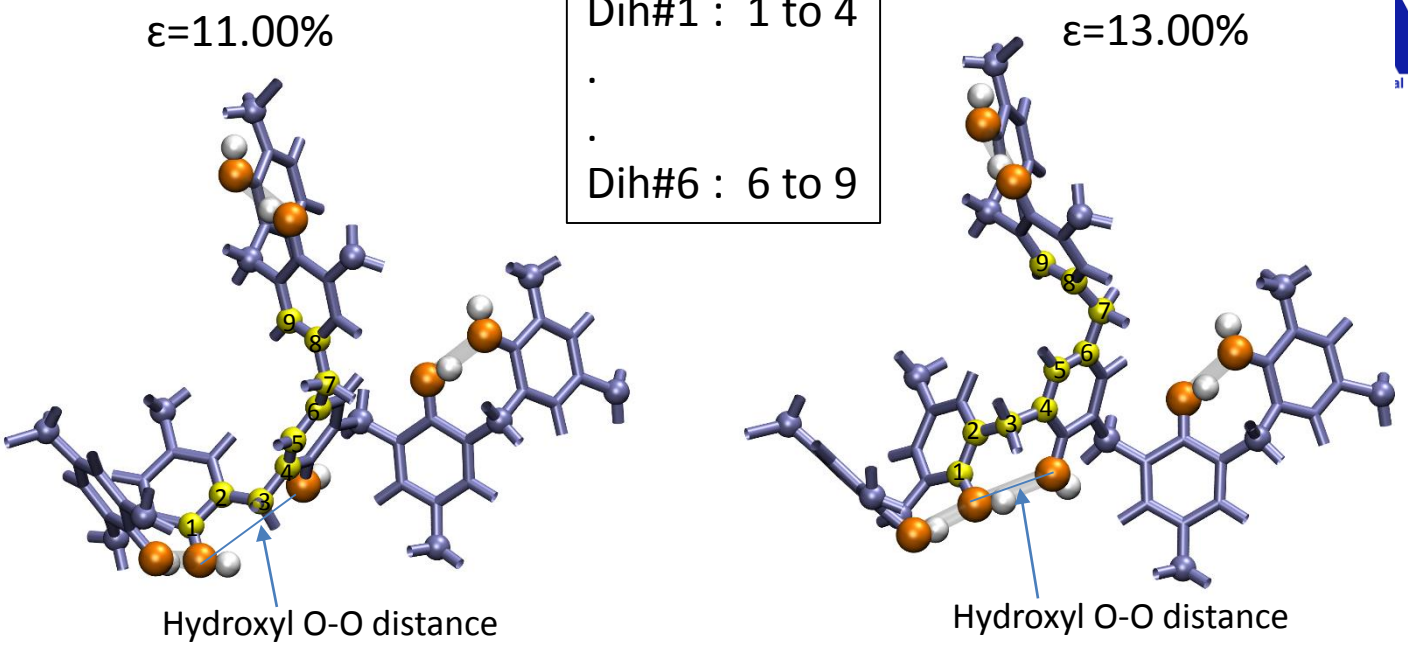
$$\sigma_y = \frac{\sqrt{3}}{2}\frac{0.077}{1-\nu^2} E_{T^*=0} + \beta T \quad (3)$$

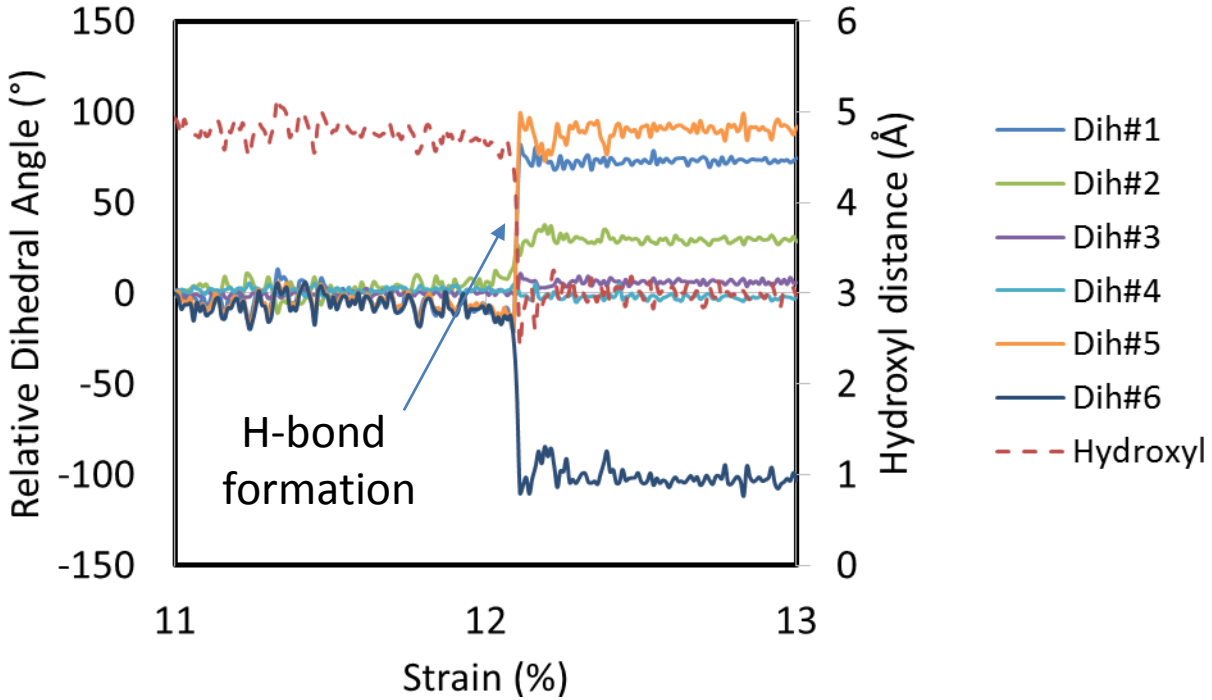


*Kambour, R., Polymer communications, 1983. 24(10): p. 292-296.

+Sundararaghavan, V. and A. Kumar, International Journal of Plasticity, 2013. 47: p. 111-125.


Percentage of Broken Bonds (%)
16
14
12
10
8
6
4
2
0
0.0
0.2
0.4
0.6
0.8
1.0
z/L
ε=173%
ε=121%
ε=57%


ε=11.00%
Dih#1 : 1 to 4
.
.
Dih#6 : 6 to 9
ε=13.00%
Hydroxyl O-O distance
Hydroxyl O-O distance


Relative Dihedral Angle (°)
Hydroxyl distance (Å)
Strain (%)
H-bond formation
Dih#1
Dih#2
Dih#3
Dih#4
Dih#5
Dih#6
Hydroxyl