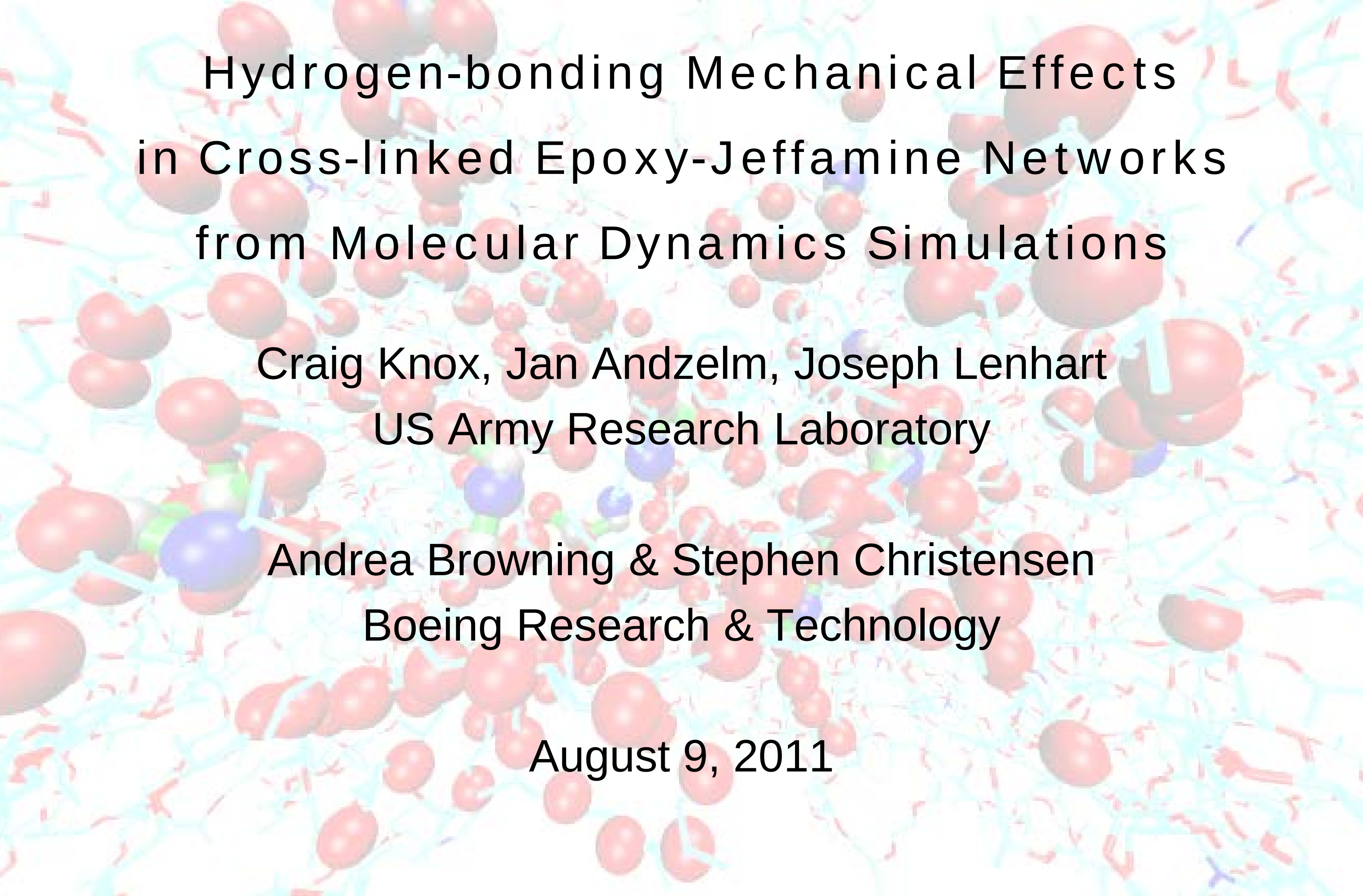

Hydrogen-bonding Mechanical Effects in Cross-linked Epoxy-Jeffamine Networks from Molecular Dynamics Simulations

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US Army Research Laboratory

Andrea Browning & Stephen Christensen
Boeing Research & Technology

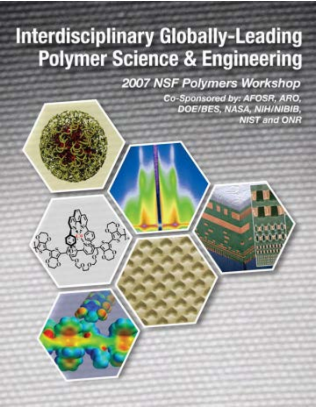
August 9, 2011

Outline

- Motivation/Background
- Methods
- Results
- Summary

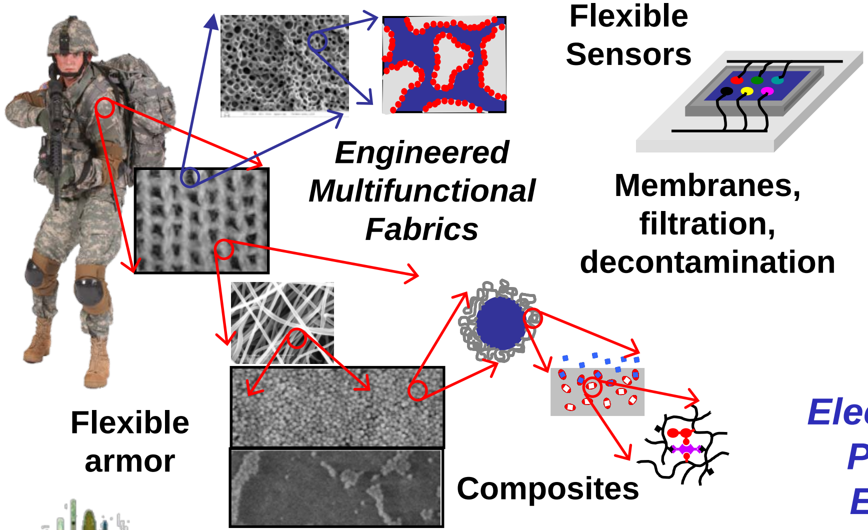
Motivation/Background

Why Polymer Networks?



- “Polymers arguably represent the most important class of materials today; their multiple and tunable attributes underpin expanding use across most advanced technology platforms.”
  - Quoting from the report of a recent polymers workshop hosted by NSF and cosponsored by AFOSR, ARO, ONR, DOE, NASA, NIH, NIST and *Macromolecules* (2009) **42**(2) 465
- Polymer networks are **pervasive in military systems**

Soldier Protection



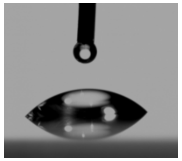
Flexible Sensors

Engineered Multifunctional Fabrics

Membranes, filtration, decontamination

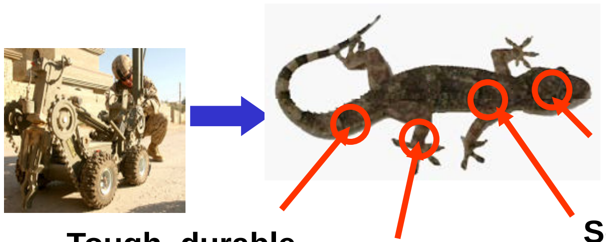
Flexible armor

Composites



Coatings

Robotics



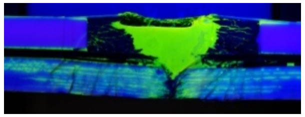
Integrated soft sensors electronics

Tough, durable, soft “body”

Controllable adhesion

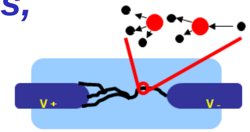
Soft actuators, “artificial muscles”

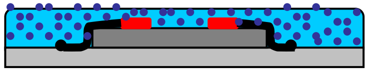
Vehicles



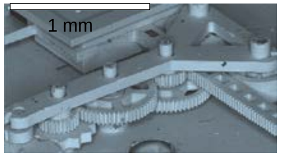
Armor / structure

Electronics, Power, Energy





Device Encapsulation

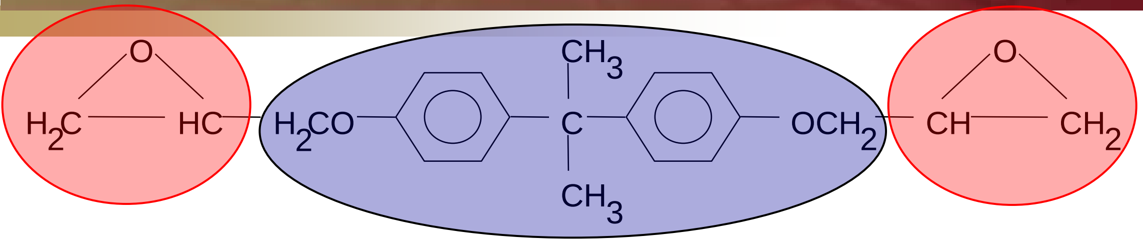


Weapons

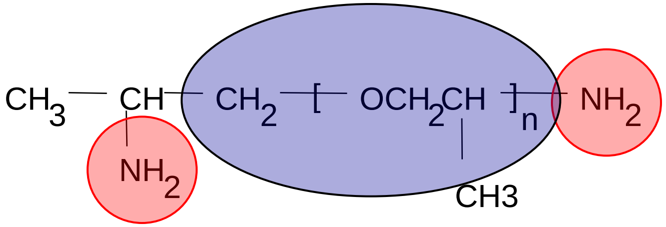
Insensitive Munitions

Low Observable Tracer Materials

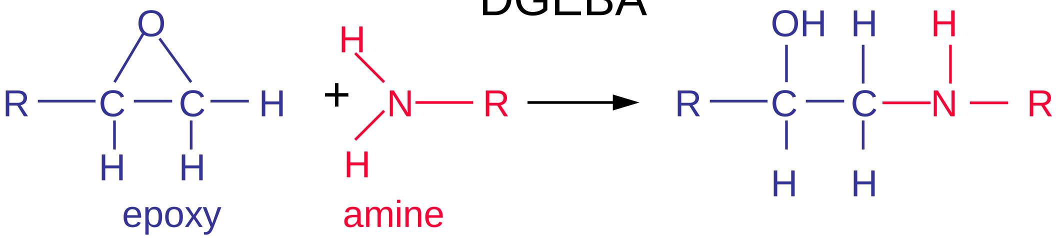
Crosslinked Polymer Networks



DGEBA

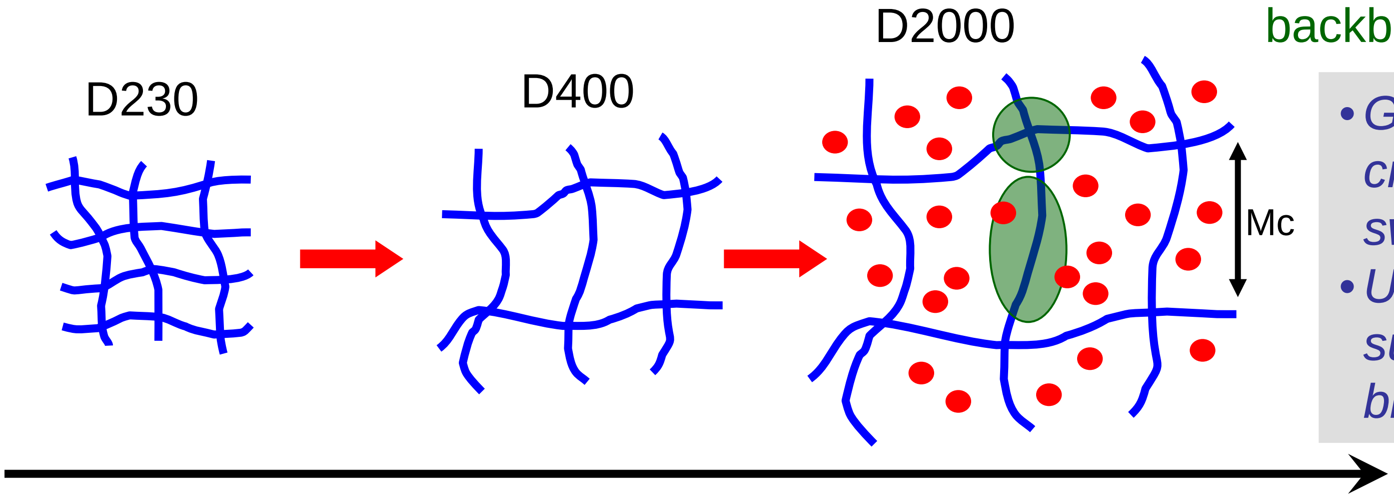


D2000, D400, D230



Mc = MW between crosslinks

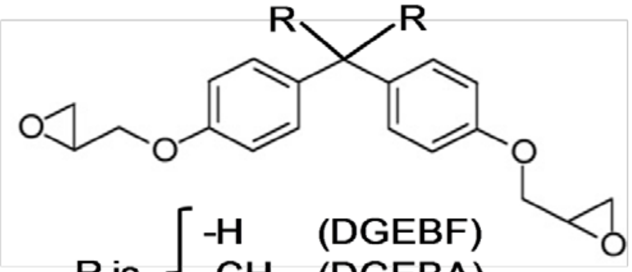
1. Chemistry & functionality (# of rxn groups per chain)
2. Spacing between rxn groups (Mc)
3. Stiffness of junctions and backbone chains



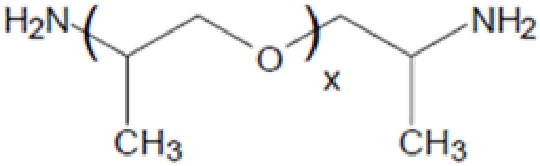
- *Gels: loosely crosslinked, solvent swollen, soft materials*
- *Useful for bio-tissue surrogates and biomedical applications*

Tg & rubbery modulus decrease; CTE & diffusion increase

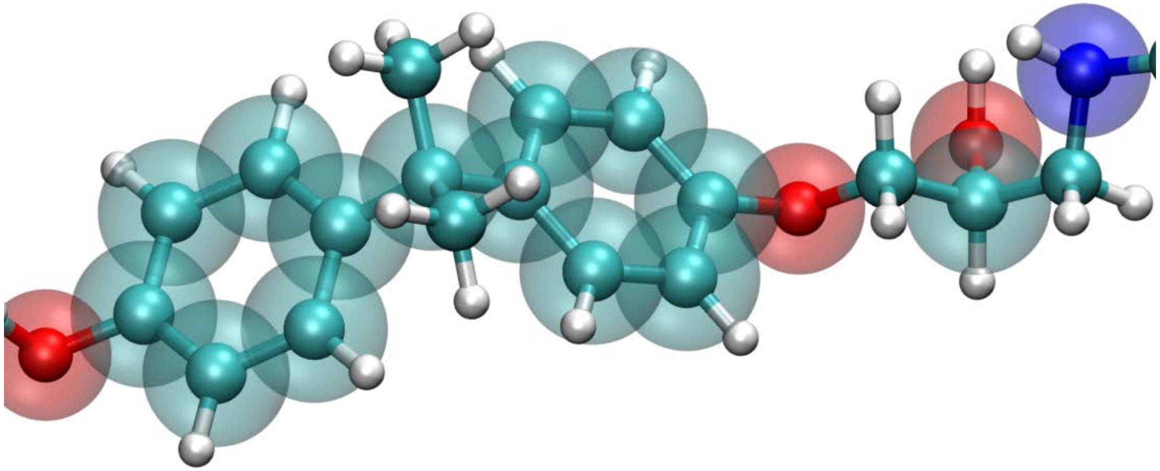
Epoxy-Jeffamine System



-R is
- -H (DGEBF)
- $-CH_3$ (DGEBA)
- $-CF_3$ (DGEBX)



JEFFAMINE®	**x**	**MW***
D-230	~2.5	230
D-400	~6.1	430
D-2000	~33	2,000
D-4000 (XTJ-510)	~68	4,000



DMA Experiments

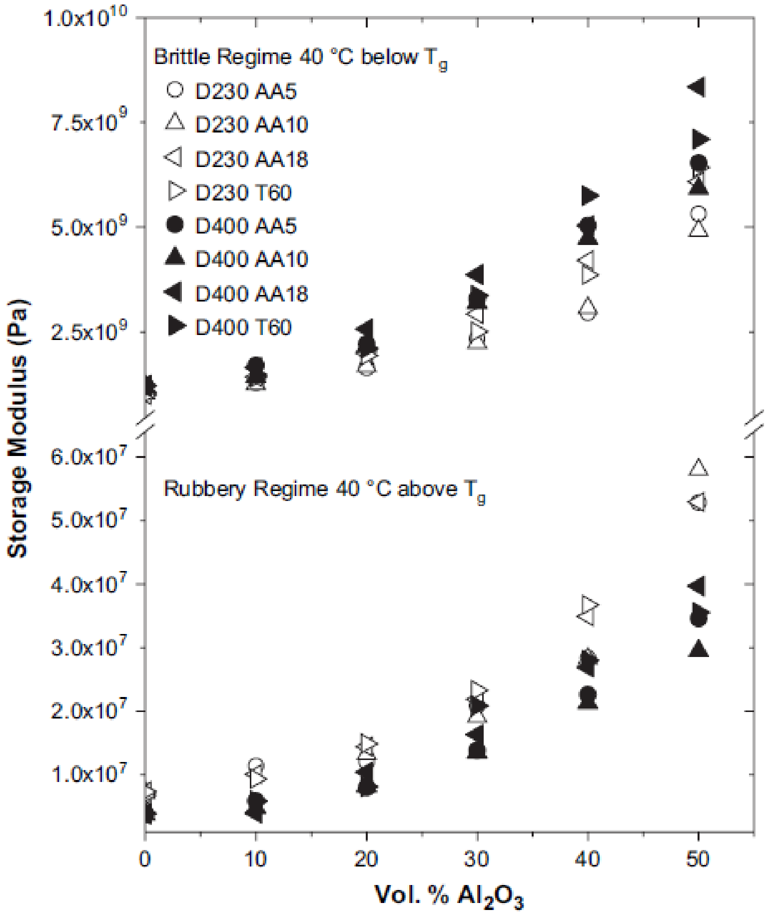
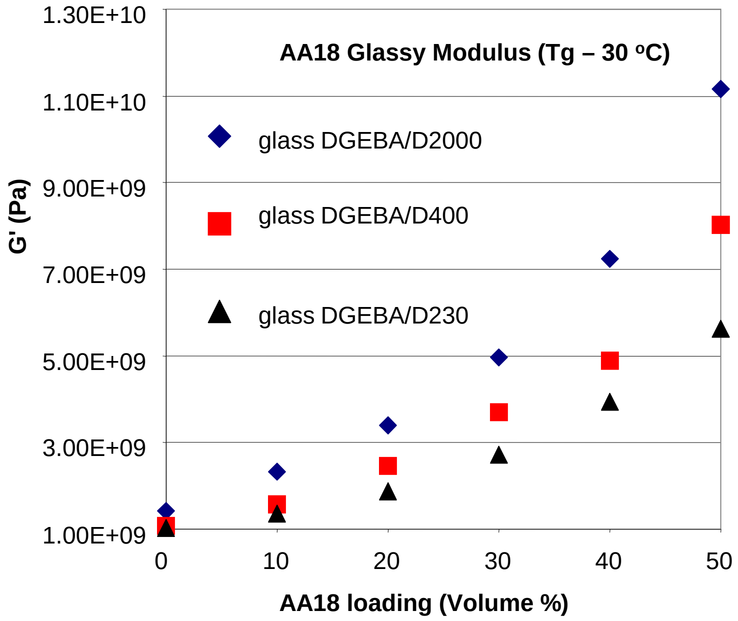
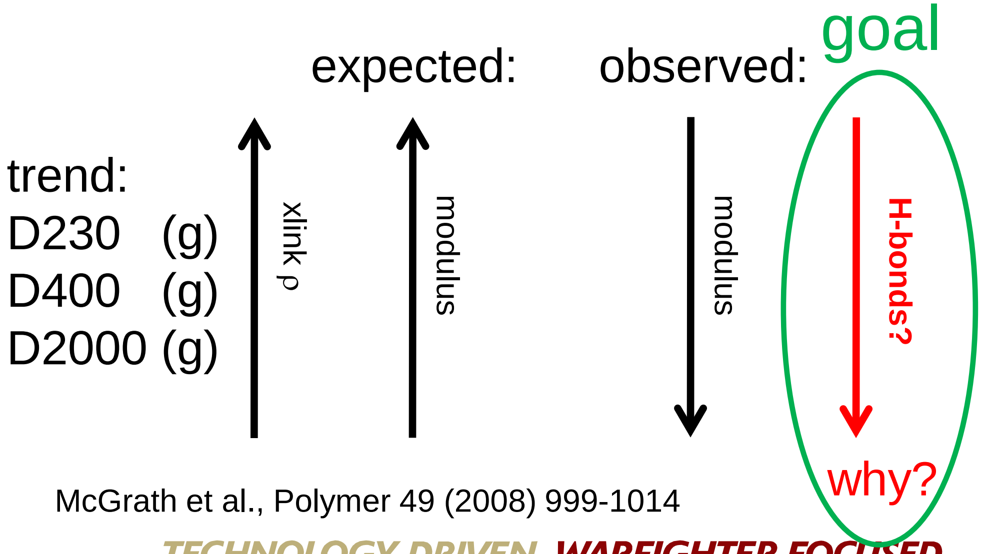


Fig. 5. (Top) the glassy modulus ($T_g - 40\,°C$) for DGEBA/D230 (open symbols) and DGEBA/D400 (closed symbols) alumina composites as a function of alumina vol.%; (bottom) the rubbery modulus ($T_g + 40\,°C$) for DGEBA/D230 (open symbols) and DGEBA/D400 (closed symbols) alumina composites as a function of alumina vol.% and particle type. The error is ±10% and was determined by multiple sample measurements.





McGrath et al., Polymer 49 (2008) 999-1014

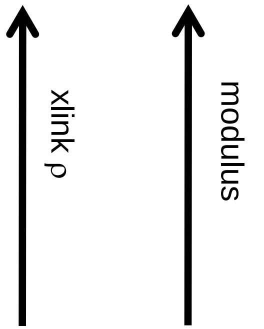
Uniaxial Tension Experiments

uni-tension
w/ Instron

strain rate =
~10^{-3} 1/s

(for ~1 cm sample size, ~2.5 mm/min / 10 mm = 4e-3 1/s)

observed:



	T_g (in °C)	Crosslink Density, ν (in moles/cc)	Glass Modulus at $T_g - 40$°C (in GPa)	Rubber Modulus at $T_g + 40$°C (in MPa)	Glass Strength at $T_g - 40$°C (in MPa)
Epon/D230	80	1.29×10^{-3}	3.1 ± 0.2	12.7 ± 2	51.2
Epon/D400	47	9.62×10^{-4}	2.4 ± 0.1	8.7 ± 0.8	60
Epon/D2000	−38	2.8×10^{-4}	1.3 ± 0.7	2	67.6

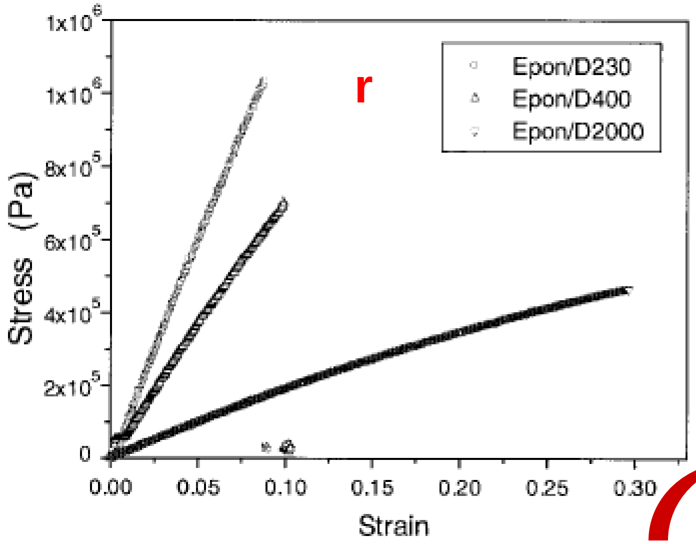


Figure 2. Stress–strain relationship at the glassy state for Epon/D230, Epon/D400, and Epon/D2000. Strain rate = 2.5 mm/min. Testing temperature are 40, 7, −78°C, respectively.

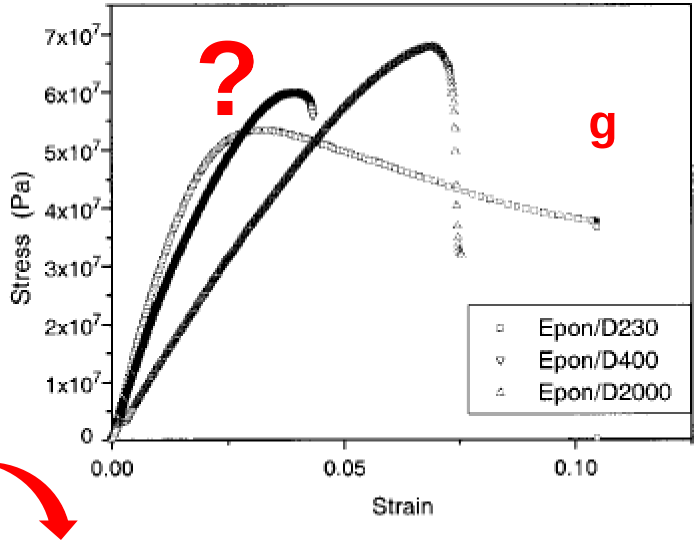


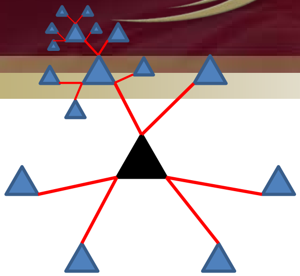
Figure 3. Stress–strain relationship at the rubbery state for Epon/D230, Epon/D400, and Epon/D2000. Strain rate = 2.5 mm/min. Testing temperatures are 120, 87, and 8°C, respectively.

contradiction?

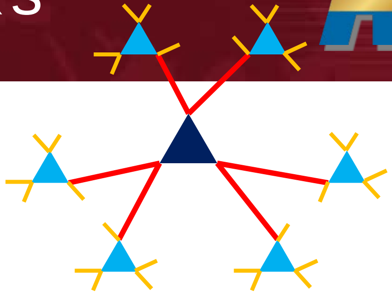
L. Shan et al., J Polym Sci B: Polym Phys, 37, 2815–2819 (1999)

Methods

Building Polymer Networks



Growing Dendrimers
(Boeing: Christensen & Browning)

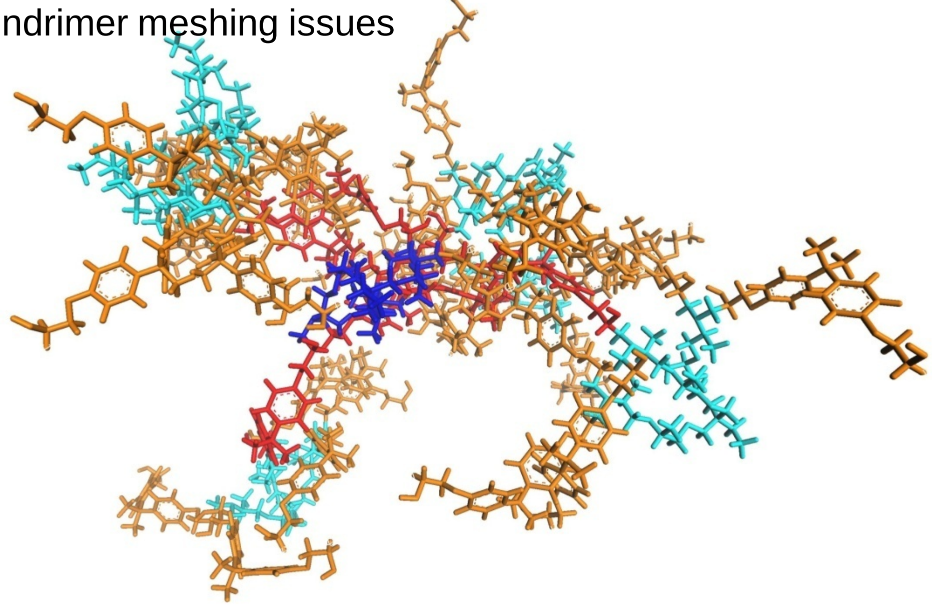


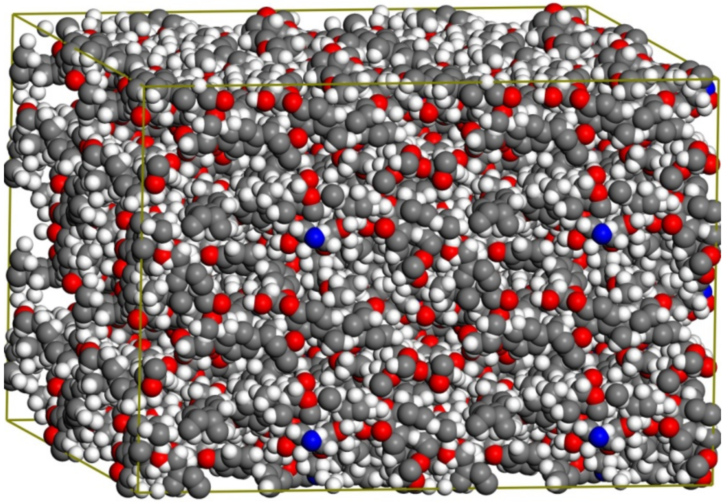
- •Build networks by growing ideal (perfect) dendrimers, then randomly modify crosslinks to add distortion/defects (dangling ends and unreacted sites) as well as to control stoichiometry

- •Pack multiple dendrimers into a box using Amorphous Cell in Materials Studio or Amorphous Builder of MAPS and then compress/anneal/equilibrate in LAMMPS

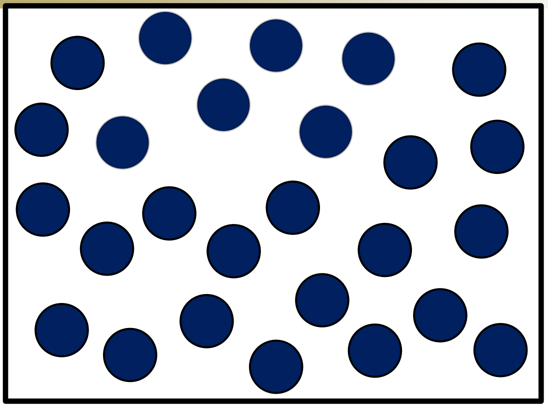
- •Pros: avoidance of artificial network strain during curing, low computational cost, availability of code

- •Cons: difficulty creating intramolecular loops and reaching very high cure; small network approx. and inter-dendrimer meshing issues

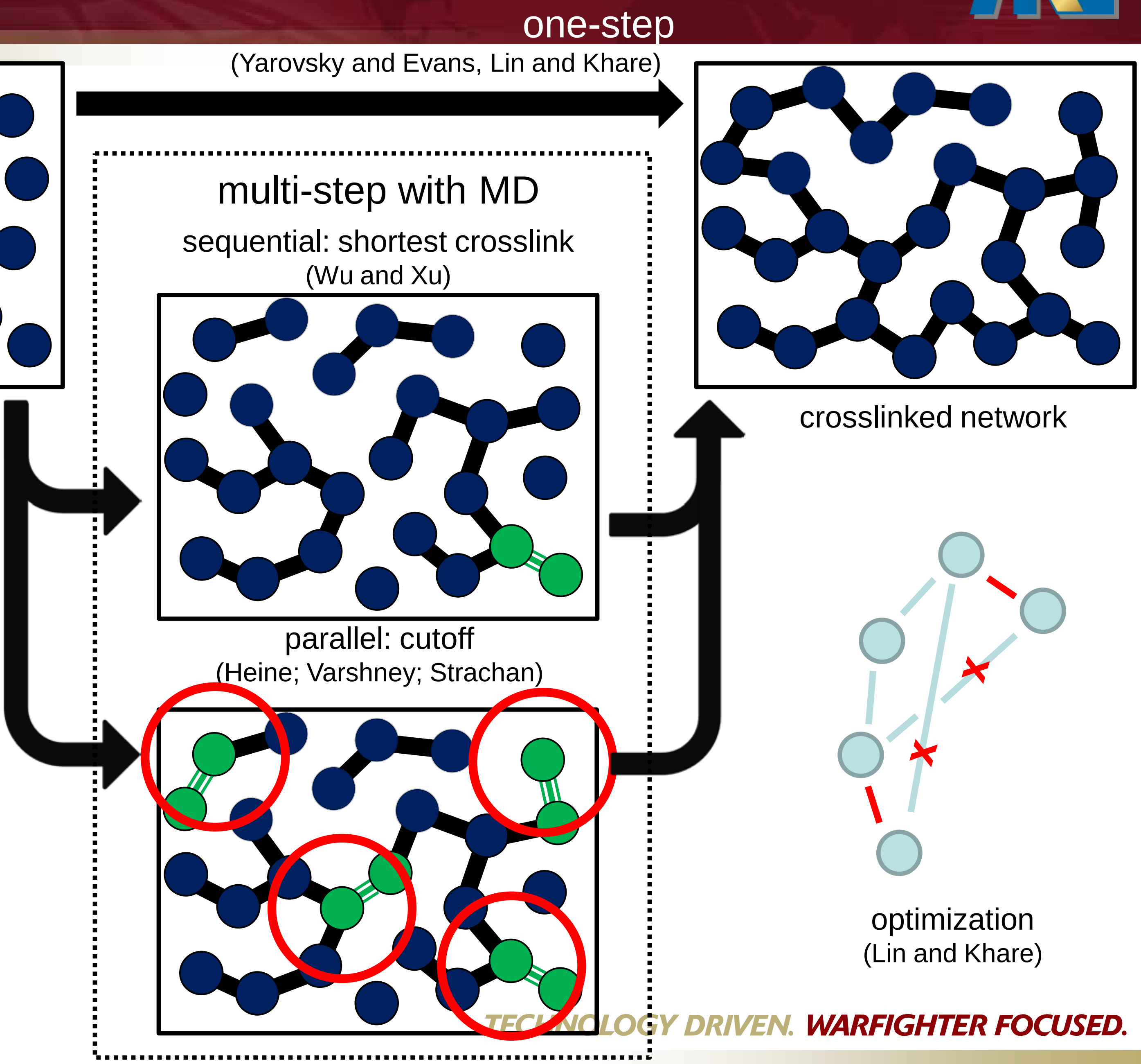




Alternative Methods: Reacting Mers



initial mix after MD



one-step

(Yarovsky and Evans, Lin and Khare)

crosslinked network

multi-step with MD

sequential: shortest crosslink

(Wu and Xu)

parallel: cutoff

(Heine; Varshney; Strachan)

optimization

(Lin and Khare)

Pros

- more realism (e.g., loops)
- complete (large) network
- chemical insight included
- up to 100% cure (difficult)

Cons

- high computational cost
- preventing artificial strain
- code complexity (changing topology and charges on-the-fly)

Method Comparison

Method	Authors	Cure	Size	Strain	Human Effort	CPU Cost	Loops	Systematic	Comments
dendrimer	Christensen	~85%	M	0	M	L	N	Y	fast and no strain no intramolecular loops small network approx.
1-step rxn	Lin and Khare	100%	L	M	L	M	Y	Y	MC optimization high cure
1-step rxn	Yarovsky and Evans	~70%	S	H	M	L	Y	Y	steric/reactivity insight big cutoff low cure
multistep rxn: sequential	Wu and Xu	~90%	S	L	L	H	Y	Y	slow kinetics issue high CPU cost
multistep rxn: parallel	Heine et al.	~90%	L	M	L	M	Y	Y	growing cutoff needed
multistep rxn: both	Varshney et al.	~90%	L	M	L	M	Y	Y	sequential or parallel rxn
multistep rxn: parallel	Li and Strachan	~80%	L	M	M	M	Y	Y	dynamic Gasteiger charge calc.

System Details

per-dendrimer counts:

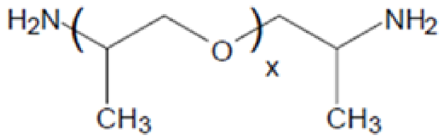
System	# of atoms	# of amine mers	# of epoxy mers	# of gens
A230	10,152	70	140	9
A2000	10,237	23	46	7
F230	9,312	70	140	9
F2000	9,961	23	46	7

stoichiometry = 2:1 (epoxy:amine)

Each system contains 8 identical copies of a dendrimer

3 dendrimer reps of each system
(each rep has unique/random cross-link topology but same mer and total cross-link counts)

Both A and F systems of a given amine have identical cross-link topology



JEFFAMINE®	x	MW*
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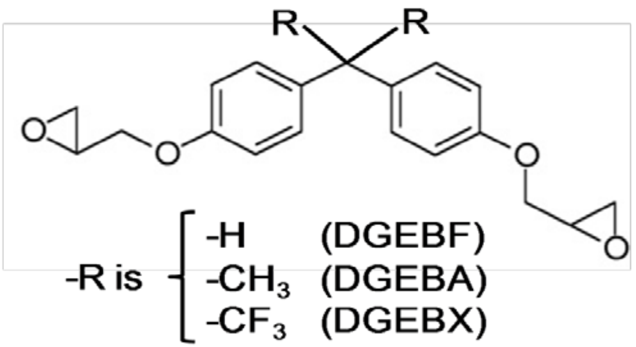
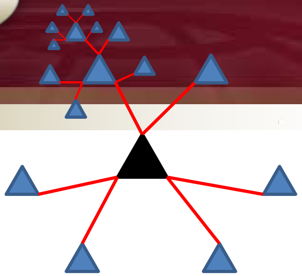


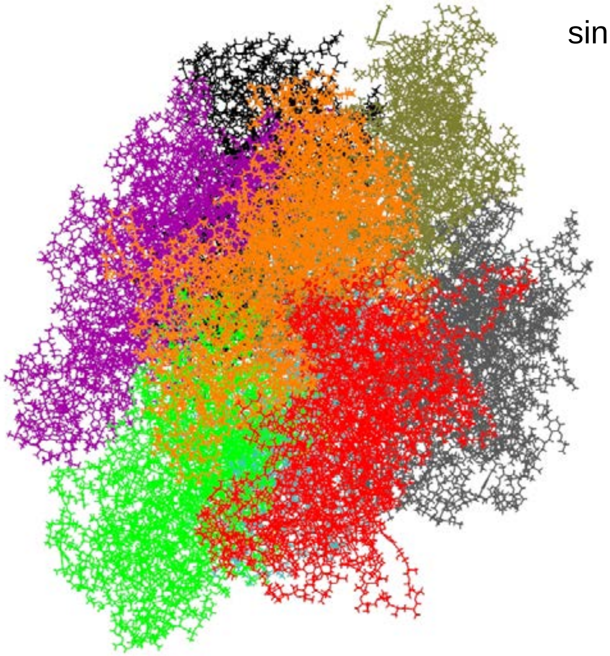
-R is
- -H (DGEBF)
- $-CH_3$ (DGEBA)
- $-CF_3$ (DGEBX)

GAFF w/ COMPASS charges

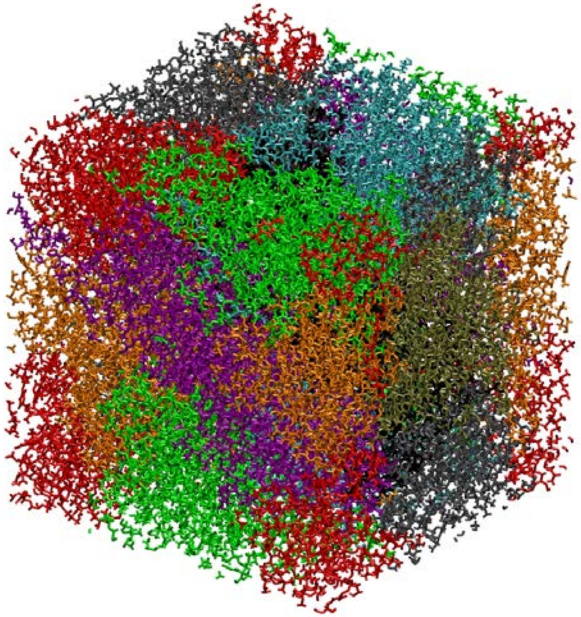
Multiple Dendrimers



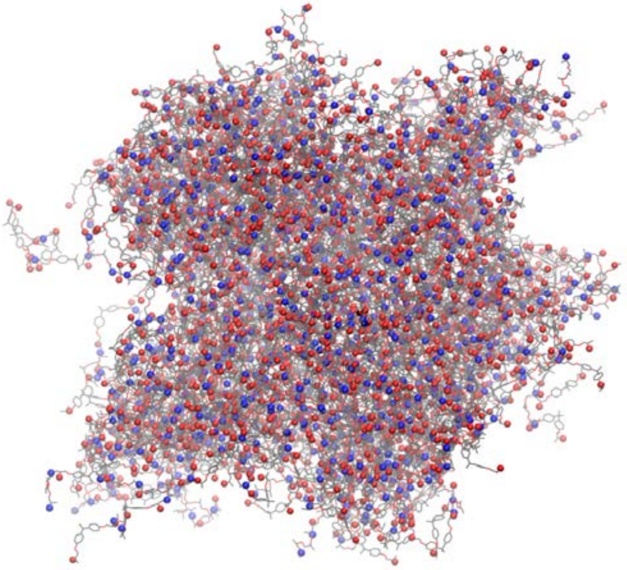
8 x 10K-atom-dendrimers



single dendrimer colored by generation



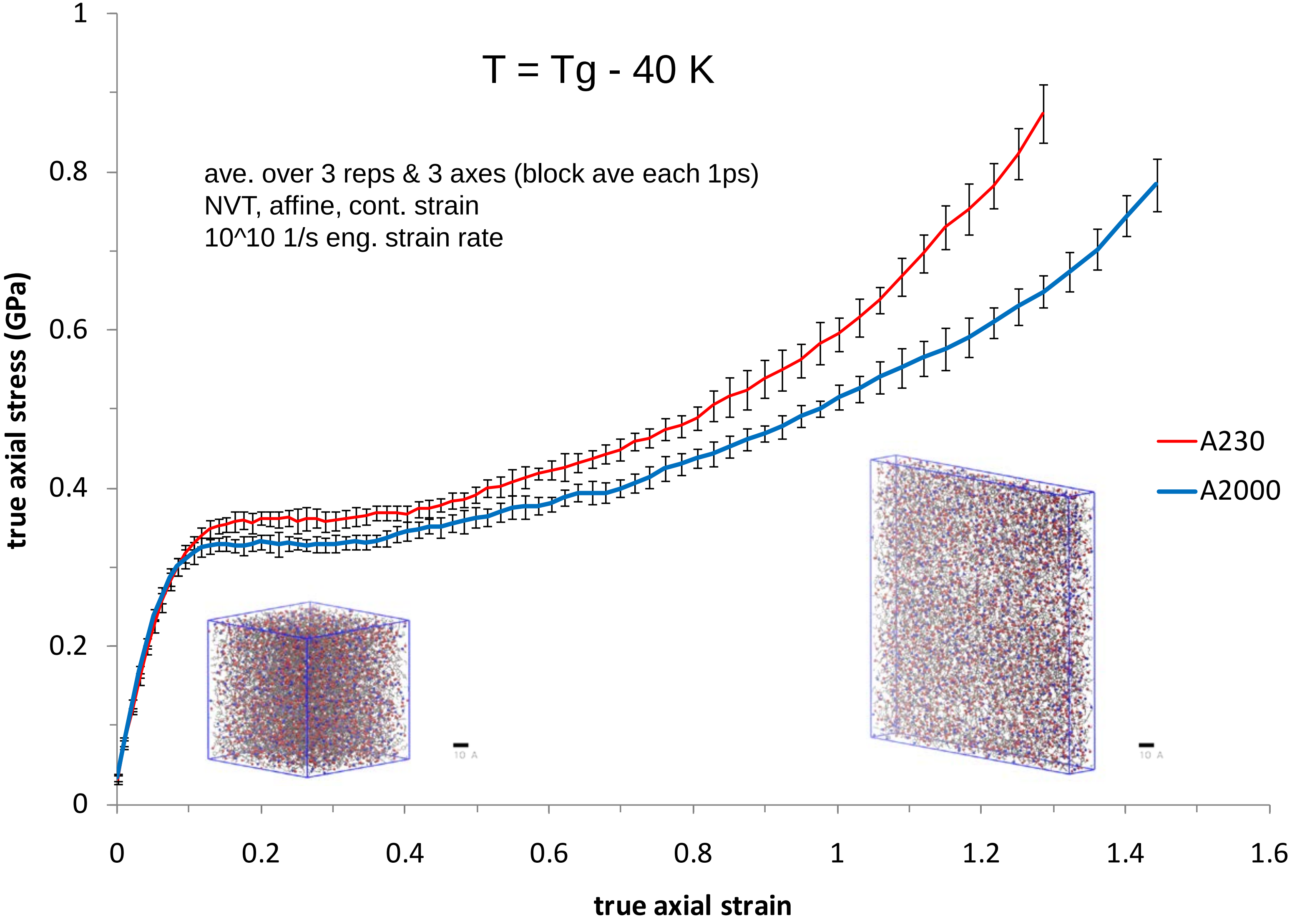
colored by dendrimer



donors (N,OH) as balls
oxygen
nitrogen
carbon
no hydrogens

Many H-bond donors and more acceptors!

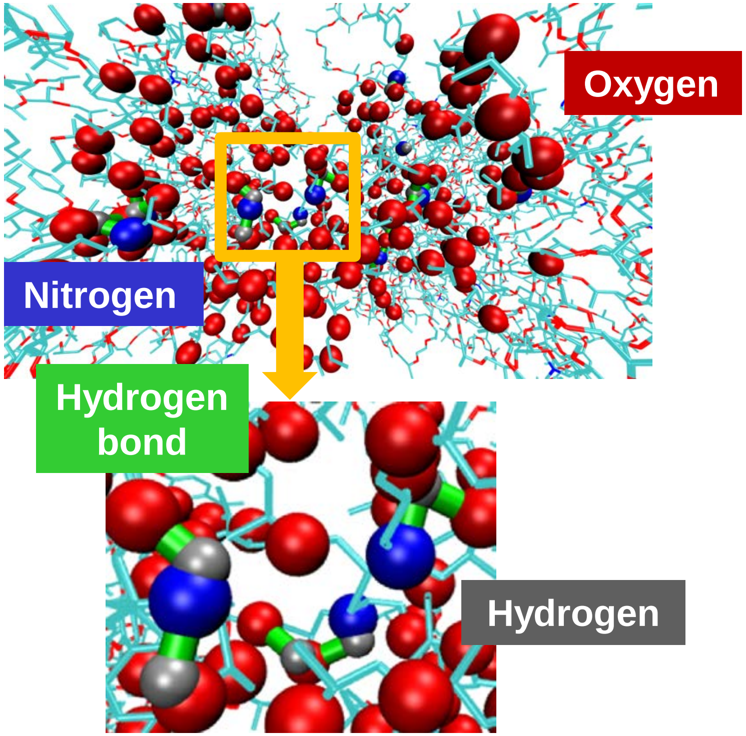
Uni-Compress Stress-Strain



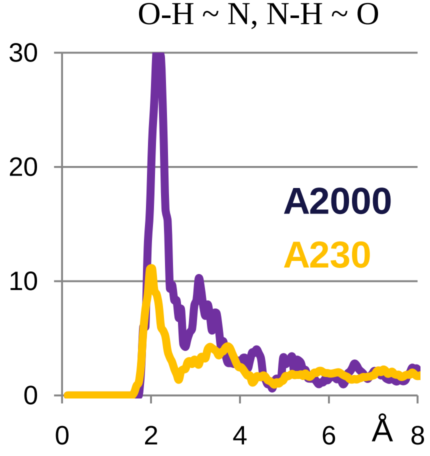
Results

H-bonding

Can H-bonding explain glassy modulus A2000 > A230 trend?



Radial Distribution Function:



More H-bonding (bigger peak) in A2000 (polymer flexibility, H-bond strength at Tg)

H-bond types:

$_{\{h\}}$O-H ~ O$_{\{ee,ea,h\}}$, 1x3=3 combinations

$_{\{h\}}$O-H ~ N$_{\{a1\text{-}3\}}$, 1x3=3

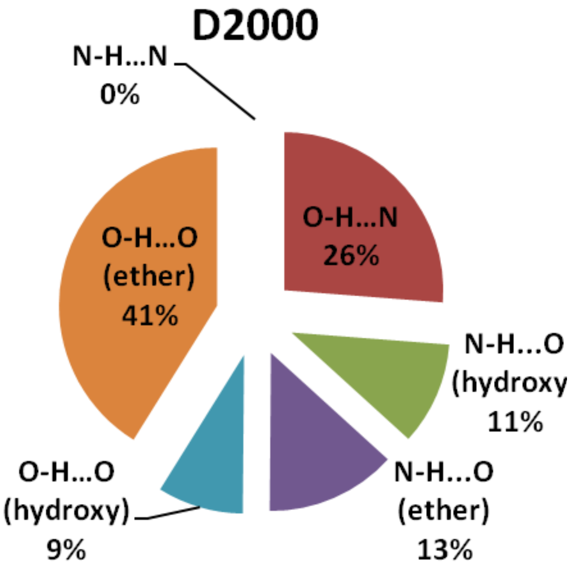
$_{\{a1\text{-}2\}}$N-H ~ O$_{\{ee,ea,h\}}$, 2x3=6

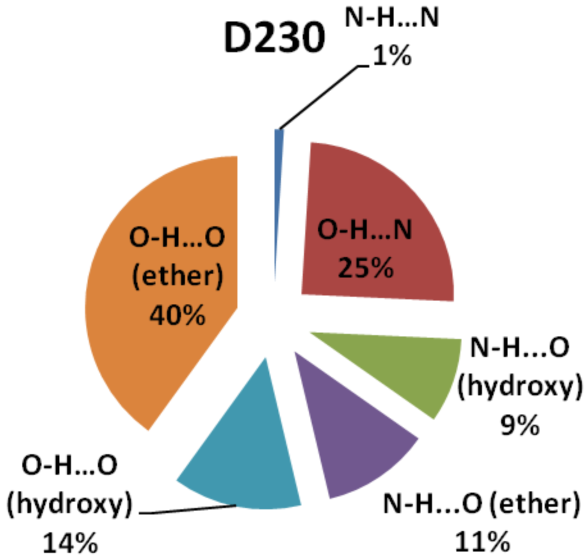
$_{\{a1\text{-}2\}}$N-H ~ N$_{\{a1\text{-}3\}}$, 2x3=6

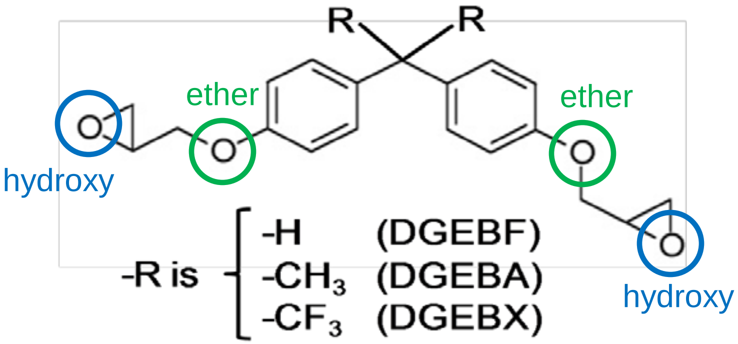
Labels of H-bonding species

Tag	Description	Proton Donor/Acceptor
a1 a2 a3	primary amine (-NH$_2$), secondary amine (-NH-), tertiary amine (-N<)	D/A D/A A
h	hydroxyl (-OH) in epoxy resin	D/A
ee	ether (-O-) in epoxy resin	A
ea	any ether in Jeffamine curing agent	A

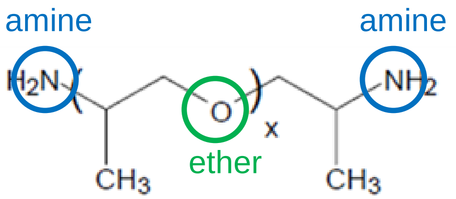
H-bonding Populations







-R is { -H (DGEBF)
-CH_3 (DGEBA)
-CF_3 (DGEBX)



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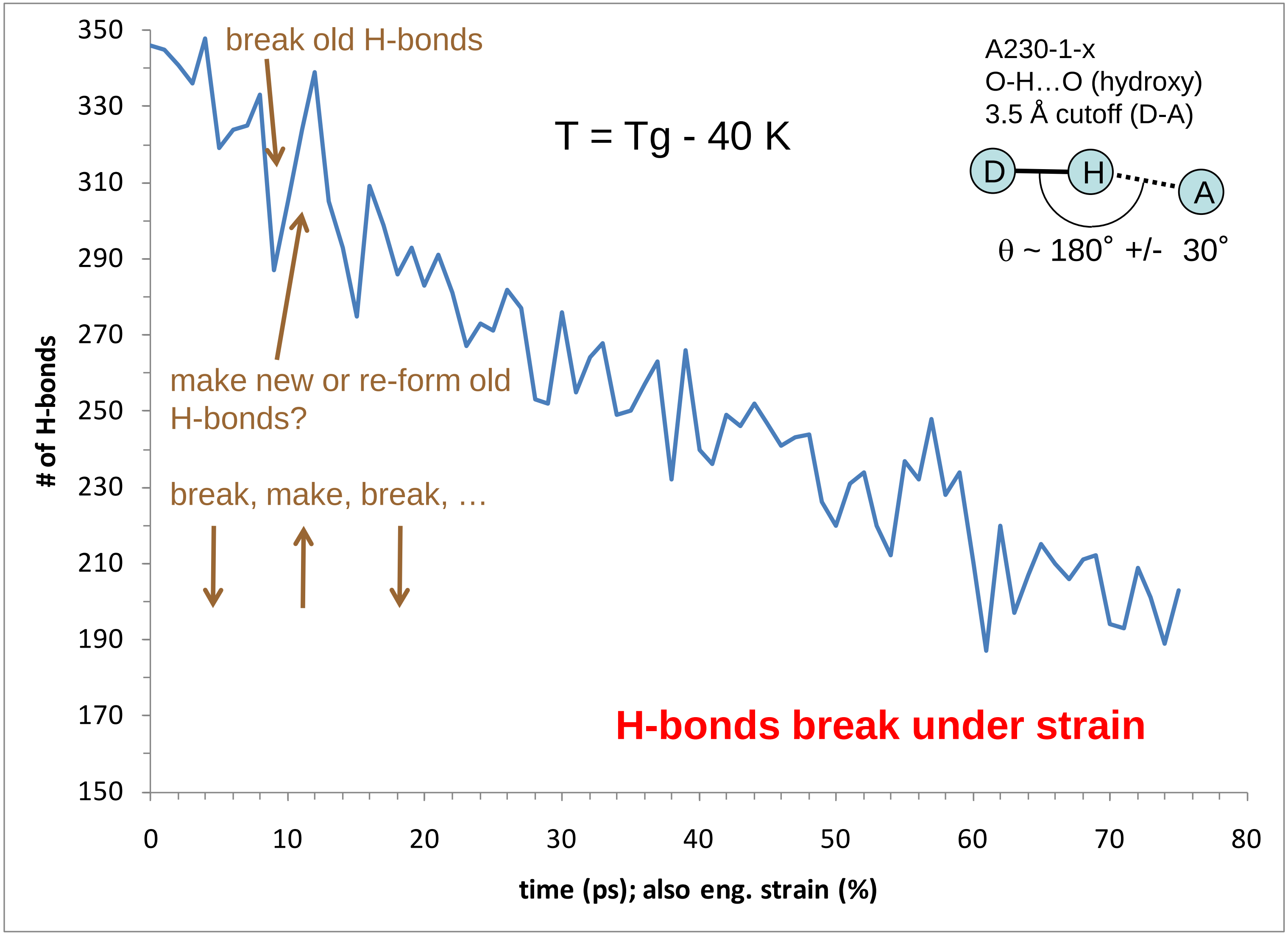
D-2000	~33	2,000
D-4000 (XTJ-510)	~68	4,000

Universal fractions of H-bond types

Breaking H-bonds



break old H-bonds

T = Tg - 40 K

A230-1-x
O-H…O (hydroxy)
3.5 Å cutoff (D-A)

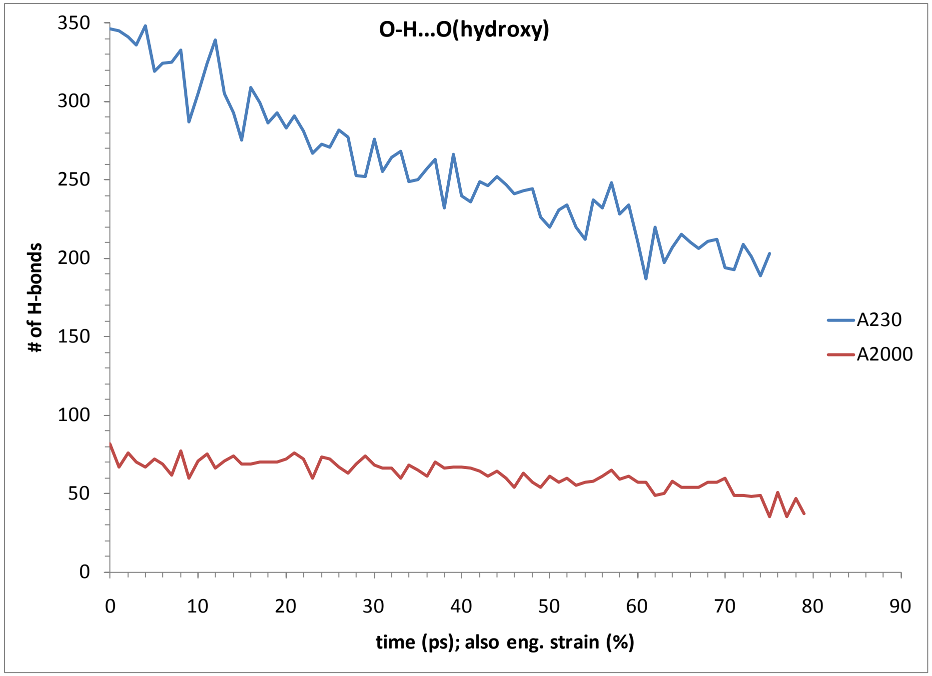
θ ~ 180° +/- 30°

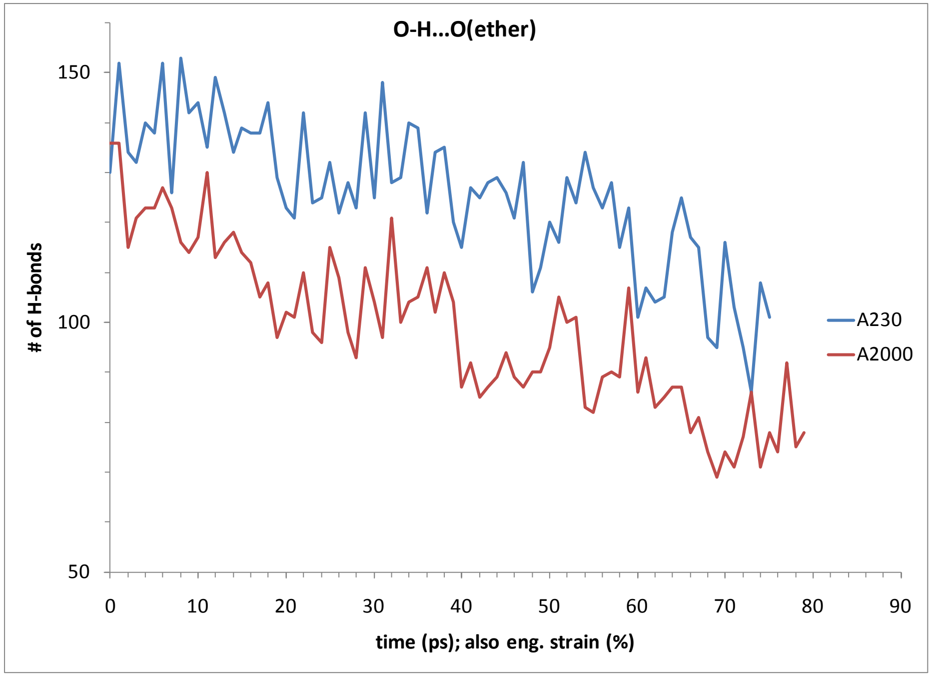
make new or re-form old H-bonds?

break, make, break, …

H-bonds break under strain

Ether and Donor Concentrations





D2000 hydroxy-ether H-bond count similar to D230 despite ~3x more donors in D230

HB & XL Toggles

Young’s modulus (GPa): **big drop in E!**

T = Tg - 40 K

Sys/Test	reg (exp)	noHB	noXL	noHB & noXL
A230	4.03 (2.25)	1.30	2.62	0.73
A2000	4.23 (3.35)	2.83	3.62	2.47
F230	3.64 (2.37)	1.03	2.34	0.38
F2000	4.05 (N/A)	2.69	3.44	2.45

noHB = no hydrogen-bonds (turn off Coulomb between all H-A pairs)

noXL = no cross-links (cut all N-C bonds & angles/dihedrals/impropers)

reg = regular (HB + XL)

exp = DMA storage modulus

Order is preserved regardless of toggle: why?
A2000 > F2000 > A230 > F230

Trends:
- A > F
- 2000 > 230 (agrees w/ DMA exp)

Observations:
- noHB and/or noXL affects 230 more than 2000
- noHB affects E more than anticipated
- noHB < noXL

NOTES:
- stdev ~ 0.1 GPa
- E = init. stress-strain slope up to 5% strain
- after 100ps NPT re-equil after toggle
- for noXL, ramp N-C VDW from 0 to full over 1st half of re-equil

H-bonding strongly affects mechanics

Stiffness from Location

Physical vs. **chemical** cross-links

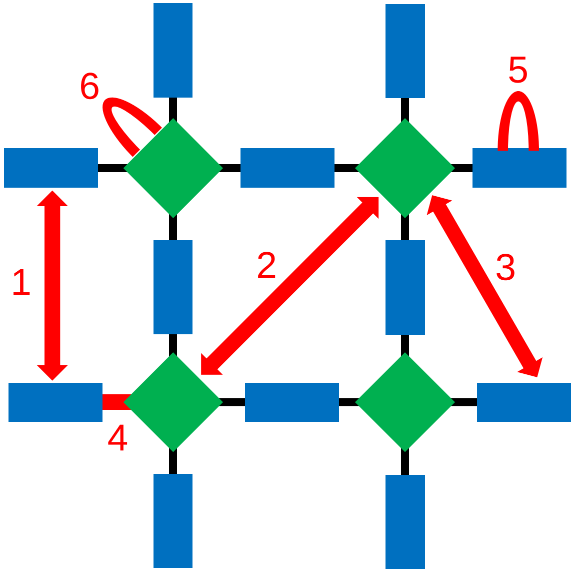
Where are H-bonds?

🟦 epoxy (e)

◆ amine (a)

⟷ H-bond

— cross-link



inter-mer:
1. e-e
2. a-a
3. e-a (no XL)
4. e-a (w/ XL)

stiffeners?

intra-mer:

5. e
6. a

Not all H-bonds are equal…

Which H-bonds increase stiffness?
Probably 1-3

inter- vs. intra-dendrimer

H-bonds may act as physical cross-links to stiffen network

Summary

✓ strain hardening in stress-strain curves, in agreement w/ exp

✓ ~1.5-2.5 GPa drop in E after turning off H-bonds

✓ H-bonding strongly affects mechanics and may be important in design

✓ A>F & 2000>230 trends in E (in agreement w/ exp), regardless of toggle (noHB,noXL)

✓ Turning off H-bonds drops E more than cutting cross-links

✓ 230 has more H-bonds per mass (or volume) but 2000 has more per donor (more effective H-bonding?)

✓ Why 2000 > 230 modulus is still unknown (entanglements/sterics?)

Acknowledgments

Ian McAninch & Andrew Schoch

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Soft System Size Requirements

“The instantaneous pressure [or stress tensor] of a simulation cell… will have mean square fluctuations (according to David Case quoting Section 114 of Statistical Physics by Landau and Lifshitz) of

$$\left\langle \delta\sigma^2 \right\rangle \sim \frac{kT}{V\beta} \sim \frac{1}{\boxed{N}}$$

, where b is the compressibility, which is RMS of roughly 100 bar for a 10,000 atom biomolecular system. Much larger fluctuations are regularly observed in practice.” (NAMD manual)

$$E = \left(\Delta\sigma \middle/ \Delta\varepsilon \right)_{meas}$$

To accurately and precisely measure elastic modulus: $\sqrt{\left\langle \delta\sigma^2 \right\rangle} << \Delta\sigma$

(stdev << magnitude)

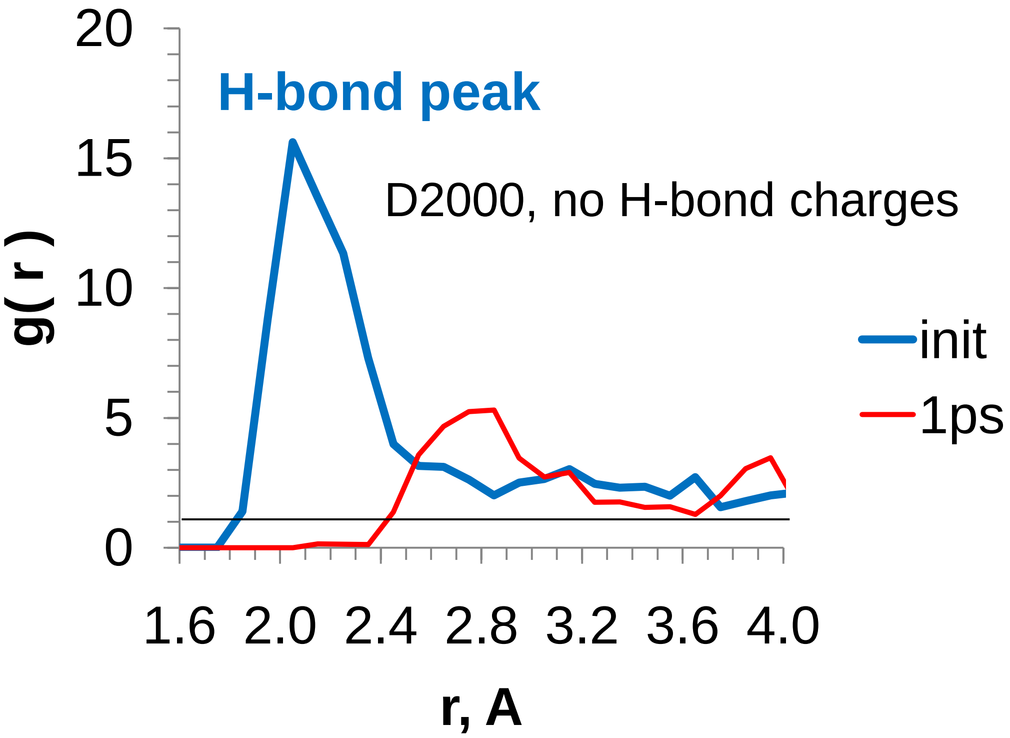
Epoxy rubbery E < ~10 MPa, so … $\Delta\sigma = E \cdot \Delta\varepsilon = (\sim 10MPa)(\sim 0.01) = 1bar$

For ~60K atoms, we measure: $\sqrt{\left\langle \delta\sigma^2 \right\rangle} \sim 30bar$

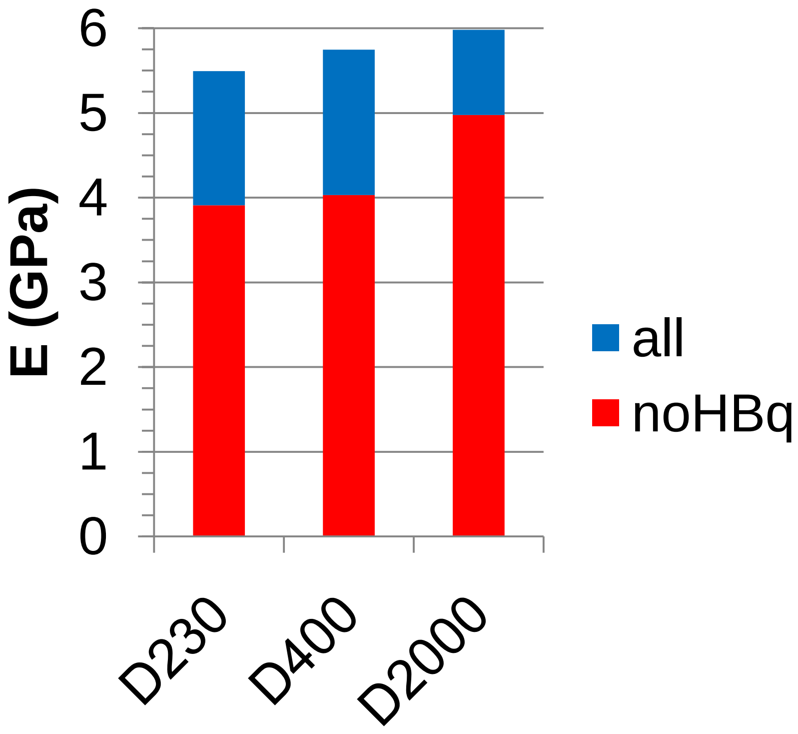
$\sqrt{\left\langle \delta\sigma^2 \right\rangle} \leq \Delta\sigma$ if $N = \dfrac{\left\langle \delta\sigma^2 \right\rangle_0}{\left\langle \delta\sigma^2 \right\rangle} \cdot N_0 = \dfrac{(30bar)^2}{(1bar)^2} \cdot (60Katoms) = \boxed{54Matoms!}$

Turning Off H-bonds (no H charge)

H-O,N (-OH,-NH$_x$, x = 0,1,2)



glassy: T – Tg = -200 K



~1.5 GPa drop without H-bonds

H-bond Energetics

(D,H,A), E_{min} (kcal/mol), r_{HA} (A), $\theta_{D\text{-}H\text{-}A}$ (degrees)

1 (OH, HO, OH): (-2.29559, 1.85, 180)
2 (OH, HO, N): (-1.63628, 1.95, 180)
3 (OH, HO, NH): (-2.46018, 1.9, 180)
4 (OH, HO, NH2): (-3.40286, 1.85, 180)
5 (OH, HO, OE1): (-0.718034, 2, 180)
6 (OH, HO, OE2): (-1.23032, 1.9, 180)
7 (NH, HN, OH): (11.1487, 4, 180)
8 (NH, HN, N): (10.8725, 4, 180)
9 (NH, HN, NH): (14.189, 4, 180)
10 (NH, HN, NH2): (17.5055, 4, 180)
11 (NH, HN, OE1): (3.97717, 4, 180)
12 (NH, HN, OE2): (6.27921, 4, 180)
13 (NH2, HN, OH): (17.6293, 4, 180)
14 (NH2, HN, N): (17.195, 4, 180)
15 (NH2, HN, NH): (22.4308, 4, 180)
16 (NH2, HN, NH2): (27.6666, 4, 180)
17 (NH2, HN, OE1): (6.30295, 4, 180)
18 (NH2, HN, OE2): (9.93722, 4, 180)

minimum combination of Donor-Hydrogen-Acceptor:

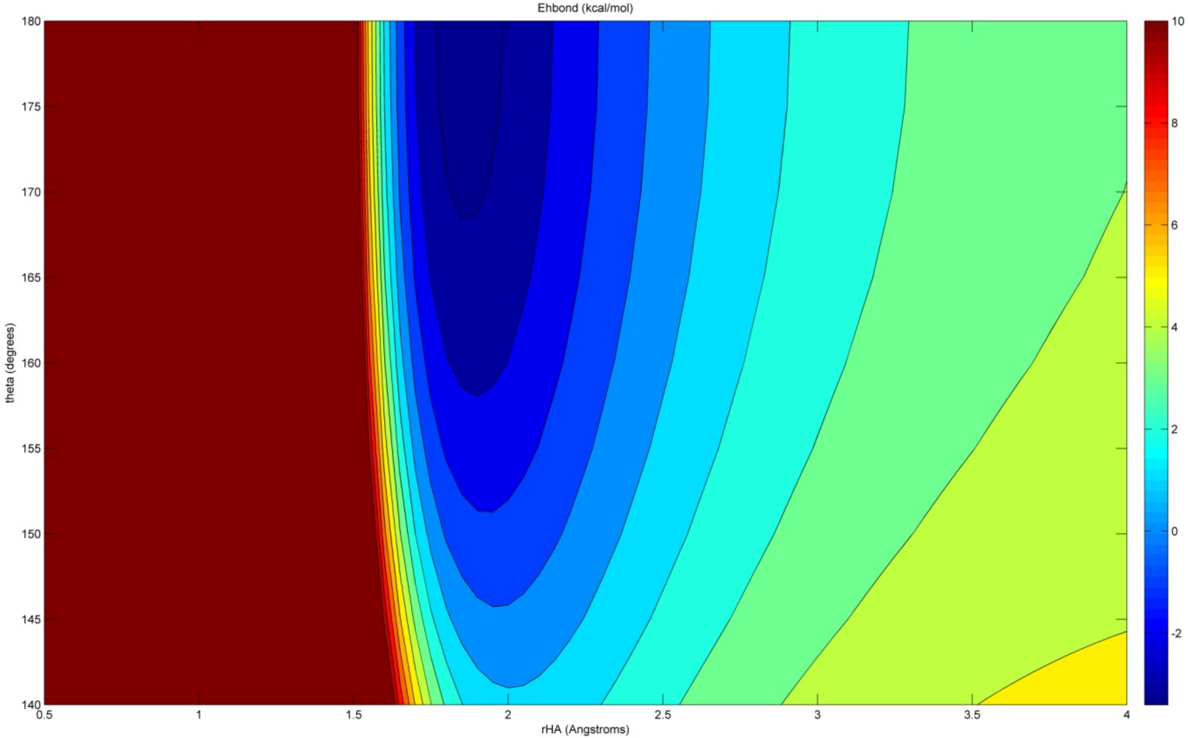
4 (OH, HO, NH2): (-3.40286, 1.85, 180)

Neglects local environment!

from MM (Coulomb + LJ of D-H…A only)

minimum in PotEng well

0.05 A Δr_{HA}, 5 deg. $\Delta\theta$ scan



Contours w/ 1 kcal/mol spacing