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

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• 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 armor
- Engineered Multifunctional Fabrics
- Flexible Sensors
- Membranes, filtration, decontamination
- Coatings

Weapons

- Insensitive Munitions
- Low Observable Tracer Materials

Vehicles

- Electronics, Power, Energy
- Device Encapsulation
- Composites

Robotics

- Integrated soft sensors electronics
- Soft actuators, “artificial muscles”

Armor / structure

1 mm
Crosslinked Polymer Networks

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

Mc = MW between crosslinks

Mc

Tg & rubbery modulus decrease; CTE & diffusion increase
Fig. 5. (Top) the glassy modulus ($T_g - 40 \, ^\circ C$) for DGEBA/D230 (open symbols) and DGEBA/D400 (closed symbols) alumina composites as a function of alumina vol.%; (bottom) the rubbery modulus ($T_g + 40 \, ^\circ C$) 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:

contradiction?

Methods
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

**one-step**

(Yarovsky and Evans, Lin and Khare)

**multi-step with MD**

sequential: shortest crosslink

(Wu and Xu)

parallel: cutoff

(Heine; Varshney; Strachan)

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)

optimalization

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

<table>
<thead>
<tr>
<th>System</th>
<th># of atoms</th>
<th># of amine mers</th>
<th># of epoxy mers</th>
<th># of gens</th>
</tr>
</thead>
<tbody>
<tr>
<td>A230</td>
<td>10,152</td>
<td>70</td>
<td>140</td>
<td>9</td>
</tr>
<tr>
<td>A2000</td>
<td>10,237</td>
<td>23</td>
<td>46</td>
<td>7</td>
</tr>
<tr>
<td>F230</td>
<td>9,312</td>
<td>70</td>
<td>140</td>
<td>9</td>
</tr>
<tr>
<td>F2000</td>
<td>9,961</td>
<td>23</td>
<td>46</td>
<td>7</td>
</tr>
</tbody>
</table>

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

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

\[ T = T_g - 40 \, \text{K} \]

Average over 3 reps & 3 axes (block ave each 1 ps)
NVT, affine, cont. strain
10^{10} \, \text{1/s eng. strain rate}

true axial stress (GPa)
true axial strain

A230
A2000
Results
H-bonding

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

Radial Distribution Function:

O-H ~ N, N-H ~ O

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_{a1-3}, 1x3=3

{a1-2} N-H ~ O_{ee,ea,h}, 2x3=6

{a1-2} N-H ~ N_{a1-3}, 2x3=6

Labels of H-bonding species

<table>
<thead>
<tr>
<th>Tag</th>
<th>Description</th>
<th>Proton Donor/Acceptor</th>
</tr>
</thead>
<tbody>
<tr>
<td>a1</td>
<td>primary amine (-NH₂),</td>
<td>D/A</td>
</tr>
<tr>
<td>a2</td>
<td>secondary amine (-NH-),</td>
<td>D/A</td>
</tr>
<tr>
<td>a3</td>
<td>tertiary amine (-N&lt;),</td>
<td>A</td>
</tr>
<tr>
<td>h</td>
<td>hydroxyl (-OH) in epoxy resin</td>
<td>D/A</td>
</tr>
<tr>
<td>ee</td>
<td>ether (-O-) in epoxy resin</td>
<td>A</td>
</tr>
<tr>
<td>ea</td>
<td>any ether in Jeffamine curing agent</td>
<td>A</td>
</tr>
</tbody>
</table>
H-bonding Populations

Universal fractions of H-bond types

D2000:
- O-H...O (ether): 41%
- O-H...N: 11%
- N-H...O (hydroxy): 9%

D230:
- O-H...O (ether): 25%
- O-H...N: 11%
- N-H...O (hydroxy): 9%

Chemical structures:

- R is [-H, -CH₃, -CF₃]
- JEFFAMINE®: D-230 (~2.5), D-400 (~6.1), D-2000 (~33), D-4000 (~68), MW: 230, 430, 2000, 4000

Technologies driven. Warfighter focused.
Breaking H-bonds

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

\[ T = T_g - 40 \, \text{K} \]

\[ \theta \sim 180^\circ \pm 30^\circ \]

- break old H-bonds
- make new or re-form old H-bonds?
- break, make, break, …

H-bonds break under strain

# of H-bonds

0 10 20 30 40 50 60 70 80

time (ps); also eng. strain (%)
D2000 hydroxy-ether H-bond count similar to D230 despite ~3x more donors in D230
**HB & XL Toggles**

**Young’s modulus (GPa):**  

<table>
<thead>
<tr>
<th>Sys/Test</th>
<th>reg (exp)</th>
<th>noHB</th>
<th>noXL</th>
<th>noHB &amp; noXL</th>
</tr>
</thead>
<tbody>
<tr>
<td>A230</td>
<td>4.03 (2.25)</td>
<td>1.30</td>
<td>2.62</td>
<td>0.73</td>
</tr>
<tr>
<td>A2000</td>
<td>4.23 (3.35)</td>
<td>2.83</td>
<td>3.62</td>
<td>2.47</td>
</tr>
<tr>
<td>F230</td>
<td>3.64 (2.37)</td>
<td>1.03</td>
<td>2.34</td>
<td>0.38</td>
</tr>
<tr>
<td>F2000</td>
<td>4.05 (N/A)</td>
<td>2.69</td>
<td>3.44</td>
<td>2.45</td>
</tr>
</tbody>
</table>

- **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

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

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

**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?

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

- intra-mer:
  5. e
  6. a

inter- vs. intra-dendrimer

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

Not all H-bonds are equal…

Which H-bonds increase stiffness?
Probably 1-3

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

- Strain hardening in stress-strain curves, in agreement with experiment.
- ~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 with experiment), 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

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LAMMPS, VMD, Materials Studio, MAPS
Thanks
"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

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

, 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)

$$E = \left( \frac{\Delta\sigma}{\Delta\epsilon} \right)_{\text{meas}}$$

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

(stdev << magnitude)

Epoxy rubbery $E < \sim 10$ MPa, so … $\Delta\sigma = E \cdot \Delta\epsilon = (\sim 10\,\text{MPa})(\sim 0.01) = 1\,\text{bar}$

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

$$\sqrt{\langle \delta\sigma^2 \rangle} \leq \Delta\sigma \quad \text{if} \quad N = \frac{\langle \delta\sigma^2 \rangle}{\langle \delta\sigma^2 \rangle_0} \cdot N_0 = \frac{(30\,\text{bar})^2}{(1\,\text{bar})^2} \cdot (60\,\text{Katoms}) = 54\,\text{Matoms!}$$
Turning Off H-bonds (no H charge)

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

H-bond peak

D2000, no H-bond charges

\[ g(r) \]

\( r, \text{Å} \)

~1.5 GPa drop without H-bonds

glassy: \( T - T_g = -200 \text{ K} \)

E (GPa)

all

noHBq
### H-bond Energetics

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

<table>
<thead>
<tr>
<th>Combination</th>
<th>$E_{\text{min}}$ (kcal/mol)</th>
<th>$r_{HA}$ (Å)</th>
<th>$\theta$ (degrees)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 (OH, HO, OH)</td>
<td>-2.29559</td>
<td>1.85</td>
<td>180</td>
</tr>
<tr>
<td>2 (OH, HO, N)</td>
<td>-1.63628</td>
<td>1.95</td>
<td>180</td>
</tr>
<tr>
<td>3 (OH, HO, NH)</td>
<td>-2.46018</td>
<td>1.9</td>
<td>180</td>
</tr>
<tr>
<td>4 (OH, HO, NH2)</td>
<td>-3.40286</td>
<td>1.85</td>
<td>180</td>
</tr>
<tr>
<td>5 (OH, HO, OE1)</td>
<td>-0.718034</td>
<td>2</td>
<td>180</td>
</tr>
<tr>
<td>6 (OH, HO, OE2)</td>
<td>-1.23032</td>
<td>1.9</td>
<td>180</td>
</tr>
<tr>
<td>7 (NH, HN, OH)</td>
<td>11.1487</td>
<td>4</td>
<td>180</td>
</tr>
<tr>
<td>8 (NH, HN, N)</td>
<td>10.8725</td>
<td>4</td>
<td>180</td>
</tr>
<tr>
<td>9 (NH, HN, NH)</td>
<td>14.189</td>
<td>4</td>
<td>180</td>
</tr>
<tr>
<td>10 (NH, HN, NH2)</td>
<td>17.5055</td>
<td>4</td>
<td>180</td>
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<td>11 (NH, HN, OE1)</td>
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<td>12 (NH, HN, OE2)</td>
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<td>17.6293</td>
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<td>180</td>
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<td>16 (NH2, HN, NH2)</td>
<td>27.6666</td>
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<td>180</td>
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<td>6.30295</td>
<td>4</td>
<td>180</td>
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<td>18 (NH2, HN, OE2)</td>
<td>9.93722</td>
<td>4</td>
<td>180</td>
</tr>
</tbody>
</table>

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 Å $\Delta r_{HA}$, 5 deg. $\Delta \theta$ scan

Contours w/ 1 kcal/mol spacing