It’s Not Easy Being Green
Bio-Inspired Design & Green Chemistry

Tom McKeag 02-21-18
Berkeley Center for Green Chemistry
1. Prevent waste

2. Maximize atom economy

3. Less hazardous chemical syntheses

4. Safer chemicals and products

5. Safer solvents and reaction conditions

6. Increase energy efficiency

7. Use renewable feedstocks

8. Avoid chemical derivatives (protecting groups)

9. Use catalysts

10. Design chemicals and products to degrade after use

11. Analyze in real time to prevent pollution

12. Minimize potential for accidents

Anastas and Warner (1998)
Plastic fiber blades to simulate those of natural grass

Infill to support the fiber blades and provide cushion

Perforated carpet backing to hold the fiber blades and allow vertical drainage

Artificial turf
Finish stone (fine aggregate)
Base stone (coarse aggregate)
Geotextile
Perforated pipe
Compacted soil
The authors identified the “infill” as a primary concern for the environmental emissions coming from synthetic Turf.

S.L.I.P.S.
Aizenberg Lab, Wyss Institute, Harvard University
Green Chemistry

Hierarchy of Safety Controls

Eliminates the exposure before it can occur

Elimination/Substitution

Requires a physical change to the workplace

Engineering Controls

Requires worker or employer to DO something

Administrative & Work Practice Controls

Requires worker to WEAR something

Personal Protective Equipment

Increasing Effectiveness

04-12-17

Tom McKeag, Berkeley Center for Green Chemistry
Autodesk Green Resin Project
Potential harmful chemicals in the current resin

Unused resin represents a safety and disposal challenge.

Unused remains unreacted after printing.

CAUTION
HAZARDOUS WASTE

20-30%
Problem: AM materials pose new threats to human health and environment

- Photoinitiator (0.4%)
- Reactive Oligomers (79.55%)
- Reactive Monomer (19.88%)
- UV-blocker (0.16%)

Reproductive toxicant
Eye irritant
Skin irritant
Aquatic toxicant
Skin sensitizer
It is possible to improve existing resin formulations

- Make sure it can’t be absorbed.
- Make sure it can breakdown quickly.

Tom McKeag, Berkeley Center for Green Chemistry
There are trade-offs to consider when optimizing the current generation of resins.

The relationship between molecular weight and viscosity.
# How do we evaluate chemical hazard?

<table>
<thead>
<tr>
<th>Hazard</th>
<th>4</th>
<th>3</th>
<th>2</th>
<th>1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sensitization</td>
<td>known resp.</td>
<td>suspected resp. / known skin</td>
<td>susp. skin</td>
<td>probably not</td>
</tr>
<tr>
<td>Acute Toxicity</td>
<td>very high</td>
<td>high</td>
<td>moderate</td>
<td>low</td>
</tr>
<tr>
<td>Carc. / Mutag.</td>
<td>known</td>
<td>suspected</td>
<td>possible</td>
<td>probably not</td>
</tr>
<tr>
<td>ED, Repr. / Dev.</td>
<td>known</td>
<td>suspected</td>
<td>possible</td>
<td>probably not</td>
</tr>
<tr>
<td>Environ./Chronic Tox.</td>
<td>very high</td>
<td>high</td>
<td>moderate</td>
<td>low</td>
</tr>
<tr>
<td>Persist / Bioacc.</td>
<td>very persist. and bioacc.</td>
<td>very persist.</td>
<td>moderately persist. and bioacc.</td>
<td>low persist. and bioacc.</td>
</tr>
</tbody>
</table>
# Autodesk acrylates

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
</tr>
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<tr>
<td>Sensitization</td>
<td>2</td>
<td>3</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
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<tr>
<td>Acute Toxicity</td>
<td>1</td>
<td>2</td>
<td>1</td>
<td>2</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>Carc./Mutag.</td>
<td>1</td>
<td>1</td>
<td>DG</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>ED, Repr. / Dev.</td>
<td>1</td>
<td>1</td>
<td>DG</td>
<td>DG</td>
<td>2</td>
<td>DG</td>
</tr>
<tr>
<td>Environ./Chroni c Tox.</td>
<td>3</td>
<td>3</td>
<td>DG</td>
<td>DG</td>
<td>DG</td>
<td>2</td>
</tr>
<tr>
<td>Persist / Bioacc.</td>
<td>2</td>
<td>2</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

**A** = SR494, **B** = SR454, **C** = Ebecryl 8210, **D** = Genomer 1122, **E** = Triproylene Gylcol Diacrylate, **F** = Tricyclodecane Dimethanol Diacrylate
Autodesk Green Resin Project

Material Feedstocks

**Types**
- Minerals
- Polysaccharides
- Proteins
- Synthetics

**Examples**
- Clay
- Chitosan
- Collagen
- Poly(ethylene glycol) PEG
Autodesk Green Resin Project

Model Applications

04-12-17

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Key Attributes

• LIFE CYCLE ASSESSMENT
  - Sourcing
  - Manufacturing
  - Recycling
  - Biodegradability

• DIRECT USE HAZARD
  - Resin
  - Polymerized Object
  - Biocompatibility
Example Two:

**Poly(glycerol sebacate acrylate) PGSA**

- **Glycerol & sebacic acid**
- **acrylates**

*Application of glue to the patch*
Example Three:

Chitosan Hydrogel
Example Three:

Modified Chitosan used in micro SLA crossed with azidobenzoic acid

*Az-chitosan*

Photo-crosslinked *Az-chitosan* hydrogel

*Biomacromolecules, 2011, 12 (1), pp 57–65*  
**DOI:** 10.1021/bm101004r
Biological Patterns


- Unity within Diversity
- Systems Approach
- Environment as Activator
- Self Organization
- Bottom-up Construction
- Hierarchy across linear scales
- Functionally graded materials
- Composite Construction
- Controlled Sacrifice
- Water is the Universal Medium
Can You Solve a Problem Across Linear Scales?

Hierarchical structure of exoskeleton of lobster
Problem Definition

• WHAT
  • Patterned Phase Change
  • Through molecular cross-linking
  • Activated by the energy of UV light

• WHAT’S WRONG
  • Incomplete Polymerization
  • Small molecules too easily taken into body
  • Products do not break down
Translation

• Cross-linking in Nature
  • Proteins, sugars as feedstock
  • Enzymes as activators

• Example: Mussel
  • Keratin proteins, polyphenols
  • pH change of acidic proteins activated by contact with more base seawater
  • Forms metal-catechol complexes
Design Process

1. What can nature tell us about patterned phase change?

2. What material and design properties are important to consider?

3. What improvements and drawback do our alternatives present?
Range of Actionable Strategies

**Approach 1:** Replace the Photoinitiator
- **Strategy A:** Curcumin & Riboflavin

**Approach 2:** Modify Acrylate-based Resins
- **Strategy B:** Triglycerides
- **Strategy C:** Chitosan

**Approach 3:** pH Photoinitiated Resins
- **Strategy D:** Calcite
- **Strategy E:** Metal Catechol Complex
Approach Three

pH Change activates organic or inorganic feedstock

CO$_3^{2-}$ CO$_3^{2-}$
Ca$^{2+}$
Ca$^{2+}$ CO$_3^{2-}$
CO$_3^{2-}$ Ca$^{2+}$

Liquid Solution

Solid Crystal Lattice

04-12-17

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<table>
<thead>
<tr>
<th>Current Product: EMBER PR48 Resin</th>
<th>Human Health Group I</th>
<th>Human Health Group II</th>
<th>Environmental Health</th>
<th>Environmental Fate</th>
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<tbody>
<tr>
<td></td>
<td>Carcinogenicity</td>
<td>Mutagenicity</td>
<td>Reproductive Toxicity</td>
<td>Developmental Toxicity</td>
</tr>
<tr>
<td>Oligomer 1: Almen Ebecryl 820</td>
<td>U</td>
<td>U</td>
<td>HH</td>
<td>HH</td>
</tr>
<tr>
<td>Oligomer 2: Santomer SR 494</td>
<td>U</td>
<td>U</td>
<td>HH</td>
<td>HH</td>
</tr>
<tr>
<td>Reactive diluent: Ruhrtex 1121</td>
<td>U</td>
<td>LH*</td>
<td>U</td>
<td>U</td>
</tr>
<tr>
<td>Photoinitiator: Esotech TPO+</td>
<td>U</td>
<td>LH</td>
<td>HH</td>
<td>HH</td>
</tr>
<tr>
<td>UV blocker: Maypo OB+</td>
<td>U</td>
<td>U</td>
<td>U</td>
<td>U</td>
</tr>
<tr>
<td><strong>Strategies</strong> A: CURCUMIN &amp; RIBOFLAVIN</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Curcumin</td>
<td>LH</td>
<td>LH</td>
<td>U</td>
<td>U</td>
</tr>
<tr>
<td>Riboflavin</td>
<td>U</td>
<td>U</td>
<td>U</td>
<td>LH*</td>
</tr>
<tr>
<td><strong>Strategies</strong> B: TRIGLYCERIDES</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acrylic (Chloride)</td>
<td>U</td>
<td>U</td>
<td>MH*</td>
<td>MH*</td>
</tr>
<tr>
<td>Triglyceride Acrylate Monomer</td>
<td>U</td>
<td>U</td>
<td>MH*</td>
<td>MH*</td>
</tr>
<tr>
<td><strong>Strategies</strong> C: METHYLCHLOROSAN</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Glycidyl Methacrylate</td>
<td>U</td>
<td>HH*</td>
<td>U</td>
<td>U</td>
</tr>
<tr>
<td>Methacrylated Glycid Chitosan</td>
<td>U</td>
<td>MH*</td>
<td>U</td>
<td>U</td>
</tr>
<tr>
<td><strong>Strategies</strong> D &amp; E: PHOTONITRATED RESINS</td>
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<td></td>
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<tr>
<td>Calcium</td>
<td>U</td>
<td>LH*</td>
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<td>U</td>
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<td>L-dihydroxyphenylalanine (Levodopa)</td>
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<td>U</td>
<td>HH</td>
<td>U</td>
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<tr>
<td>Ketoprofen</td>
<td>U</td>
<td>U</td>
<td>U</td>
<td>MH</td>
</tr>
<tr>
<td>DBN [1,5-diazacyclo[4.5.0]non-5-one]</td>
<td>U</td>
<td>U</td>
<td>U</td>
<td>HH</td>
</tr>
<tr>
<td>Phenylglycine acid</td>
<td>U</td>
<td>U</td>
<td>U</td>
<td>MH*</td>
</tr>
<tr>
<td>Phenethylamine</td>
<td>U</td>
<td>U</td>
<td>U</td>
<td>MH</td>
</tr>
<tr>
<td>Strategy</td>
<td>A: New Photo-initiators</td>
<td>B: Triglyceride acrylates</td>
<td>C: Glycol Chitosan acrylates</td>
<td>D: Calcite Resin</td>
</tr>
<tr>
<td>--------------------------</td>
<td>-------------------------</td>
<td>---------------------------</td>
<td>-----------------------------</td>
<td>------------------</td>
</tr>
<tr>
<td>Skin sensitization</td>
<td></td>
<td>□</td>
<td>□</td>
<td>□</td>
</tr>
<tr>
<td>Eye Irritation</td>
<td></td>
<td>□</td>
<td>□</td>
<td>□</td>
</tr>
<tr>
<td>Skin Irritation</td>
<td></td>
<td>□</td>
<td>□</td>
<td>□</td>
</tr>
<tr>
<td>Aquatic Toxicity</td>
<td></td>
<td>□</td>
<td>□</td>
<td>□</td>
</tr>
<tr>
<td>Reproductive Toxicity</td>
<td></td>
<td>□</td>
<td>□</td>
<td>□</td>
</tr>
</tbody>
</table>

**KEY:**  
- □: Data Gaps  
- □: Identified Hazard  
- □: Decreased Hazard
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymerization</td>
<td>Initiation is possible, as confirmed by Autodesk and Greener Solutions researchers.</td>
<td>Propagation and termination may be affected by larger monomer size, proportion of uncured resin could increase.</td>
<td>Propagation and termination may be affected by larger monomer size. Uncured resin could increase. Methacrylates are less reactive than acrylates.</td>
<td>PBGs active enough to initiate precipitation? Propagation occurs in many marine organisms. Termination occurs when solution returns to equilibrium.</td>
<td>Metal-catechols have been synthesized in lab using pH gradients. Propagation shown in tube worms (Stewart, 2000).</td>
</tr>
<tr>
<td>Speed</td>
<td>Much lower concentration, 0.001-0.0001%, could yield comparable speed.</td>
<td>Same as PR48</td>
<td>Slower than PR48, methacrylates less reactive.</td>
<td>PBGs require further testing in SLA system.</td>
<td>PBGs require further testing in SLA system.</td>
</tr>
<tr>
<td>Viscosity</td>
<td>Likely more viscous than PR48 (and hazard proportional to viscosity).</td>
<td>Likely more viscous than PR48, higher MW proportional to viscosity.</td>
<td>Likely more viscous than PR48.</td>
<td>Viscosity could be too low, CaCO₃ must be at extremely high concentrations.</td>
<td>Viscosity could be too low, CaCO₃ must be at extremely high concentrations.</td>
</tr>
<tr>
<td>Resolution</td>
<td>Same as PR48</td>
<td>Will require further testing in SLA</td>
<td>Will require further testing in SLA</td>
<td>Micron level precision in 2D lithography (Ito &amp; Wilson, 2009)</td>
<td>Micron level precision in 2D lithography (Ito &amp; Wilson, 2009).</td>
</tr>
<tr>
<td>Layer Adhesion</td>
<td>Same as PR48</td>
<td>Lower monomer conversion could limit adhesion, requires optimization</td>
<td>Lower monomer conversion could limit adhesion, requires optimization</td>
<td>Require optimization in Ember, CaCO₃ must be in high enough concentrations for layer growth</td>
<td>Adhesive properties of metal-catechols could cause jamming</td>
</tr>
<tr>
<td>Commercially Available</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Calcite: Yes PBGs: Some but not all</td>
<td>Calcite: Yes PBGs: Some but not all</td>
</tr>
</tbody>
</table>
**Approach:** life cycle stages inform sustainability tools

**Life Cycle Stages:**
- Raw Material Sourcing
- Processing, Manufacturing, Formulation
- Product Distribution And Use
- Disposal or Revalorization

**Tools for Measuring Sustainability:**
- RA: Risk Assessment
- SMM: Sustainable Materials Management
- LCA: Life Cycle Analysis
- GDM: Green Design Metrics
- CHA: Chemical Hazard Assessment
- WPT: Whole Product Testing

**Principles of Sustainable Design:**
- Preserve Natural Capital
- Eliminate Hazards and Pollution from Products and Processes
- Use Life-Cycle Thinking and Design with the End in Mind
What’s Next

• Collaboration with Millipore-Sigma and Autodesk to formulate SLA resin that will meet the criteria outlined in “biofriendly database”

• Incorporation of database into Autodesk’s materials database, so that EHS criteria is included in material performance intelligence software available to designers
Summary

• Bio-inspired not necessarily “biofriendly”
• EHS performance part of overall performance
• This can lead to innovation & advantage
• Models from nature can be the clearest paths to solving some of your design contradictions
Bio-Inspired Design & Green Chemistry

Tom McKeag
Berkeley Center for Green Chemistry
02-21-18
Nature’s Design Strategies
Aren’t You Smart!
Sea Cucumber
Fig. 1. Natural model and bioinspired design of chemomechanical nanocomposites.

J R Capadona et al. Science 2008;319:1370-1374
Structure of Hair

- high-S proteins
- high-tyr proteins
- low-S proteins
- left-handed coiled-coil rope
- right-handed α-helix
- matrix
- microfibril (intermediate filament)
- macrofibril
- cell membrane complex
- nuclear remnant
- para-cortical cell
- ortho-cortical cell
- meso-cortical cell
- cuticle
- exocuticle
- endocuticle
- root end

- 1 2
- 7 200
- 2,000 20,000 nm
Bone
Four Technology Trends

1. Human/Machine Interface & the internet of things

2. Mass Customization & Capability Convergence

3. Expanding Spatial Frontiers

4. Biological Paradigms
Theme Three:
Expanding Spatial Frontiers

Caltech 4D Microscope

MIT & Niels Bohr Institute
I. REPLACING THE PHOToinitiator

Strategy A: Curcumin & Riboflavin

II. MODIFYING ACRYLATE-BASED RESINS

Strategy B: Triglycerides
Strategy C: Chitosan

III. pH PHOToinitiated RESINS

Strategy D: Calcite
Strategy E: Metal Ligand Complexes
pH Change activates organic or inorganic feedstock

Liquid Solution

Solid Crystal Lattice