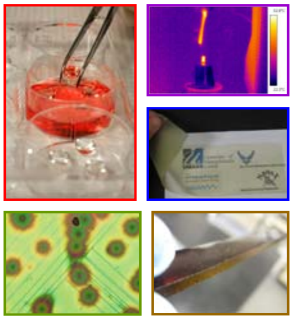
Research Summary

Associate Professor Daniel Schmidt
UML Plastics Engineering

Expertise:
Nanocomposites, thermosets, materials analysis, porous materials & sol-gel chemistry



- ***Polymer Networks***
  - *Flexible methodology for the preparation of tissue engineering scaffolds*
  - *pH-responsive hydrogels for cell culture applications*
  - *Low toxicity thiol-ene adhesives and coatings*
  - *Green binders for engineered wood products*
  - *BPA-free epoxies for can coating applications*
  - *MEMS, microelectronics and functional coatings from pre-ceramic polymers*
  - *Reworkable thermosets for wind energy*
- ***Hybrid Materials***
  - *Polymer nanolaminates*
  - *Structure / properties relations in model polymer / layered silicate nanocomposites*
  - *Industrial applications of polymer nanocomposites (packaging, HFFR, etc.)*
- ***Materials Analysis***
  - *Assessing deformation mechanisms via thermal tensile testing*
  - *Rapid screening of nanomaterial toxicity*

Safer Alternatives: What's on the Horizon

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A Brief Introduction

- Many types of adhesives exist
  - Natural, naturally derived, synthetic
  - Solvent-borne, water-borne, high solids
- Not all adhesives are toxic or dangerous, but there is clearly room for improvement
- Schmidt Group research efforts:
  - Replacing bisphenol A (BPA) in epoxy resins
  - Developing new thiol-ene adhesives

Practical, High-Performance BPA-Free Epoxy Resins

R. Romano & D. F. Schmidt, supported by:

- Massachusetts Toxics Use Reduction Institute (TURI)
- University of Massachusetts Commercial Ventures & Intellectual Property Technology Development Fund (UMass CVIP TDF)
- University of Massachusetts Lowell Commercial Ventures & Intellectual Property Office (UML CVIP)

Why Replace BPA?

boston.com — BPA may increase asthma risk in kids, but tough to avoid
March 1, 2013

MN: Partial BPA, formaldehyde bans considered — MINNESOTA PUBLIC RADIO
March 13, 2013

The Forecaster — ME: Freeport lawmaker joins effort to ban BPA
March 19, 2013

Spanish group campaigns for BPA ban in food contact materials — FoodProduction daily.com
March 22, 2013

Why Replace BPA?

Walla Walla Union-Bulletin.com — WA: List of Health Concerns Related to BPA Grows Longer
March 29, 2013

San Francisco Chronicle — CA: BPA may be labeled 'toxicant' by state
April 4, 2013

FoodProduction daily.com — **BPA fears may hit metal packaging sector**
April 4, 2013

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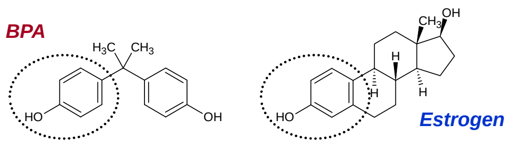
Why Replace BPA?

- BPA's structural similarities with estrogen are the issue



- BPA has been identified as an endocrine disruptor as a result

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How big a problem is it?

- Estimated annual global BPA demand:
  - 2003: ~2 million tons
  - 2006: ~4 million tons
  - 2012: ~4.7 million tons
  - 2015: ~6.3 million tons (predicted 3/2010)
- Demand breakdown in the US (2003):
  - Total: ~856,000 tons
  - Polycarbonate: ~619,000 tons (~72%)
  - Epoxy resins: ~184,000 tons (~22%)
  - Other applications: ~53,000 tons (~6%)

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How big a problem is it?

- BPA exposure is ubiquitous and constant in the industrialized world
  - Various studies show urine levels of 1-3 ng/mL
  - Typical blood levels are in the same range (vs. tens of pg/mL estrogen normally in plasma)
  - Large-scale Canadian government study (2007-2009) shows highest levels in teens (12-19), followed by children (6-11)
  - Levels recently found to be twice as high in Americans as in Canadians (*CMAJ*, doi: 10.1503/cmaj.101408)

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How big a problem is it?

- Dietary exposure appears to be significant
  - "BPA and DEHP exposures were substantially reduced when participants' diets were restricted to food with limited packaging." (*EHP*, doi:10.1289/ehp.1003170)
  - Can coatings are the most likely culprit
- Cash register receipts, recycled paper other potential sources
- Food-contact polycarbonate replaced over these concerns

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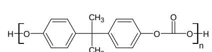
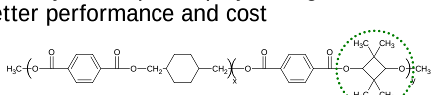
Replacing BPA in Polycarbonate

- Polycarbonate is a stiff, strong thermoplastic based on BPA

(BPA) Polycarbonate



- Recently developed copolyester gives similar / better performance and cost



Eastman's new TRITAN copolyester

- Key to success is use of new tetramethyl cyclobutanediol (CBDO) monomer

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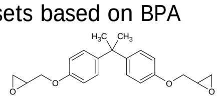
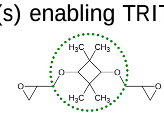
Replacing BPA in Epoxy Resins

- Most common epoxies are stiff, strong thermosets based on BPA



Bisphenol A diglydicyl ether (BADGE)

- No drop-in replacements available
- SOLUTION: Replace BPA with the same monomer(s) enabling TRITAN's success



Tetramethyl cyclobutanediol diglycidyl ether (CBDO-DGE)

Results so far…

(all but viscosity & UV data from TETA-cured networks)

Property	BPA Epoxy (high purity)	CBDO Epoxy (technical grade)

Current Activities

- International patent application filed
- Scale-up underway via epoxy toll manufacturer
  - Immediate goal is production of kg quantities of material to meet industry requests for samples to evaluate in adhesives, composites
  - Near-term goal is the preparation of “upgraded” (high molecular weight) epoxies for sampling by can coating manufacturers

Safer Adhesives via Thiol-ene Chemistry

S. Patil & D. F. Schmidt, supported by:

TURI

- Massachusetts Toxics Use Reduction Institute (TURI)

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Research Aims

- To develop a new family of all-purpose, high performance adhesives
  - Should be based on readily available, non-volatile, minimally toxic components
  - Should cure rapidly at room temperature without scorching or environmental sensitivity
  - End result should be a robust polymer network with good adhesion, physical and mechanical properties

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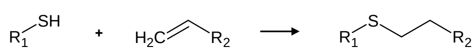
Approach

- Thiol-ene chemistry



- Reaction is specific and rapid, even at RT
- Can occur via multiple mechanisms (Michael addition vs. free radical curing)
  - Multiple means of initiating or accelerating cure
  - Less susceptible to inhibition
- Thiol-ene systems already seeing serious interest for low shrinkage photocured dental composites (Prof. Chris Bowman, CU Boulder)

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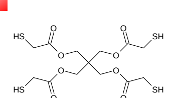
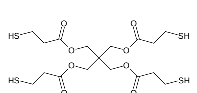
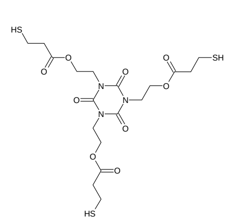
Materials: Thiol Reagents



Pentaerythritol tetrakis(2-mercaptoacetate)
(THIOCURE® PETMA, Bruno Bock)



Pentaerythritol tetrakis(3-mercaptopropionate)
(THIOCURE® PETMP, Bruno Bock)



Tris[2-(3-mercaptopropionyloxy)ethyl] isocyanurate
(TMEI)

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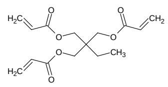
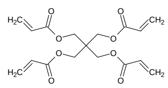
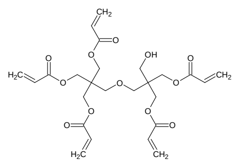
Materials: -Ene Reagents



Trimethylolpropane triacrylate
(TMPTA, Sartomer SR-351H)



Pentaerythritol tetracrylate
(PETA, Sartomer SR-295)



Dipentaerythritol pentaacrylate
(DPEPA, Sartomer SR-399)

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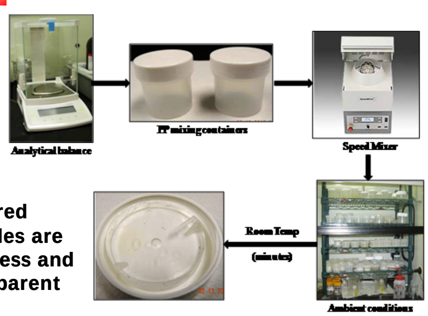
Sample Preparation



→ Cured samples are colorless and transparent

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Curing Results (RT)

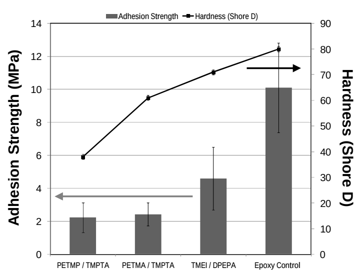
Thiol	-Ene	Catalyst	Setting time (min., approx.)	Hardness (Shore D)
PETMA	TMPTA	*n*-Hexylamine (0.25 wt%)	5	61 ± 1
PETMP	TMPTA	-	30	38 ± 1
PETMP	PETA	-	30	55 ± 1
TMEI	TMPTA	-	5	55
TMEI	PETA	-	5	60
TMEI	DPEPA	Di-*n*-propylamine (0.4 wt%)	8	71

Adhesion Strength

(lap shear, mild steel)

Thiol	-Ene	Catalyst	Adhesion strength (MPa)
PETMA	TMPTA	*n*-Hexylamine (0.25 wt%)	2.4 ± 0.7
PETMP	TMPTA	-	2.2 ± 0.9
PETMP	PETA	-	*(not measured)*
TMEI	TMPTA	-	*(not measured)*
TMEI	PETA	-	*(too fragile to test)*
TMEI	DPEPA	Di-*n*-propylamine (0.4 wt%)	4.6 ± 1.9

Adhesion vs. Hardness



- Adhesion strength to mild steel tracks with hardness
- Can increase hardness through additional composition variations

Summary

- With adhesives, focus has historically been on performance first and foremost
- Demand for safer solutions has increased substantially in more recent times
- Opportunities exist to create practical, economical, high-performance alternatives
- Two examples are given here
  - BPA-free epoxy resins
  - Thiol-ene thermosets
- Many more possibilities exist!

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What's next?

QUESTIONS

(Thanks for your attention!)