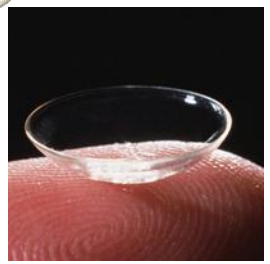
Polymers and the Industry University Cooperative Research Center on Photopolymerization

Allan Guymon

Professor and Chair

The University of Iowa
Chemical & Biochemical Engineering

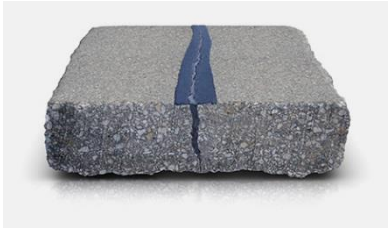


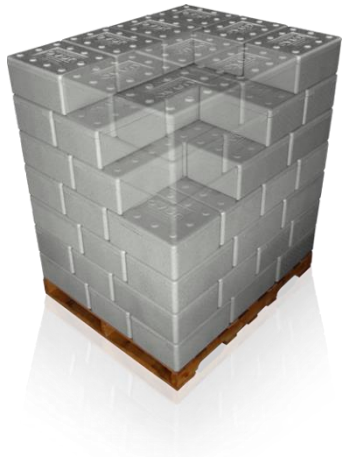
Global Warm Mix Asphalt Workshop
October 30, 2013

Asphalt, My Family, and Me

- Professor E. Park Guymon (aka Dad)
  - Chemistry Department- Weber State University
  - Heavy Oils Research
    - Great Salt Lake Oil
    - Tar Sands

- Mike Guymon – Maxwell Products
  - Foam Containers for Crack Sealant
  - Heat Exchanger
  - Crack Sealant Polymer Additives





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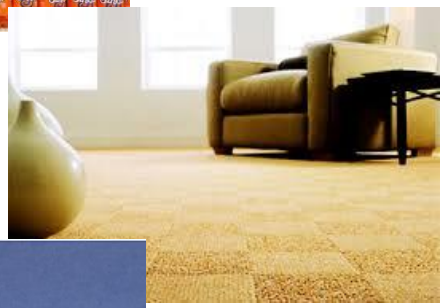
Polymers

- A polymer is a macromolecule that is made from many small molecules (monomers) joined together chemically.
- Versatile materials with a wide range of properties.
  - Plastics
  - Coatings
  - Fibers
  - Elastomers (Rubber)
  - Adhesives

Types of Polymers

- Step/Condensation Polymers
  - Polyesters
  - Nylon
  - Polycarbonate
- Chain/Addition Polymers
  - Polyethylene
  - Polystyrene
  - Poly(vinyl acetate)
  - Teflon
  - Acrylic Resins
  - Block Copolymers



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Common Polymer Additives for Asphalt

- Asphalt- Mix of Asphaltenes (polycyclic aromatic compounds) and Maltenes (higher MW oil components)
- styrene-butadiene-styrene (SBS) block copolymers (elastomeric)
- styrene-butadiene-rubber (SBR) latex (elastomeric)
- ethylene-vinyl-acetate (EVA) block copolymers (plastomeric)
- natural rubber latex (elastomeric)
- atactic polypropylene (APP) (plastomeric)
- high molecular weight waxes

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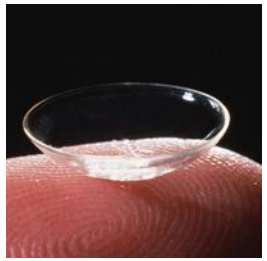
Photopolymerization – Chain Polymerization Initiated with Light

Advantages

- ⇨Rapid
- ⇨Energy Efficient
- ⇨Solvent Free
- ⇨Control of Initiation
  - •Spatial/Temporal
- ⇨Initiation Independent of Temperature



Disadvantages

- ⇨Thin Films
- ⇨ Oxygen Inhibition

Future Opportunities in Advanced Materials

C. Allan Guymon, Center (CFAP) Co-director, University of Iowa
http://css.engineering.uiowa.edu/~cfap/

Academic - Industrial Interactions:

Vision

Industrial Group, e.g. Radtech

Education, Meetings, Proposals, Lobbying

Academic Group, e.g. CFAP

Industrial Companies, e.g. Consortia

Longer Term, Broadly Focused Research, Disruptive Technologies, Predevelopment Research

Academic Group, e.g. CFAP

Industrial Company, e.g. 3M

Developmental Research, Sponsored / Focused Research, Consulting

Individual Faculty

The NSF Photopolymerizations IUCRC

- **CFAP is collaborative**
  - ➔ ***Industry and academic participants***
  - ➔ ***Focused on advancing the understanding and implementation of photopolymerization reactions***
  - ➔ ***Research, education, and meeting activities***
- **CFAP is located both at the University of Iowa and the University of Colorado with co-Directors Chris Bowman and Allan Guymon**
- **The Directors, Industrial Advisory Board, and other participants meet regularly to assure the achievement of the overall objectives**
- **Organization of Photopolymerization Fundamentals Meetings in 2002, 2005, 2007, 2009, 2011, 2013, and beyond**
- **Catalyst for European Symposium for Photopolymer Science (ESPS)**

Consortia Level Interactions

- **Research Program**
  - ➔ ***Developed from Strategic Planning, Company Solicitations, Faculty Proposals and Industrial Selection of Projects***
  - ➔ ***Faculty - Student - Industrial Scientist Feedback Loop and Mentoring***
  - ➔ ***Companies have IP Rights, Early Access to Research, and Input on Research Directions and Systems***

- **Mentoring and Training of Students by Industrial Colleagues - Committees, Seminars, Presentations, etc.**

CFAP Organization

- NSF Evaluation has placed CFAP in the top 20% of IUCRCs in nearly every category of performance and satisfaction of the various constituents
- Industrial Sponsors Pay an Annual Fee to Support Research and Heavily Leveraged Funding
- Faculty Co-Develop Proposals with Industry that Subsequently Selects from All the Proposals
- Twice per Year Meetings Provide Feedback to Ongoing Research Projects

Industrial Membership Benefits

- **Research Results**
  - ➔ ***Input into Project Selections***
  - ➔ ***Early Access to Research Results***
  - ➔ ***Royalty-free License to Center IP***
- **Interaction with Leading Photopolymerization Scientists and Engineers from Academia *and* Industry**
- **Access to State-of-the-Art Facilities**
- **Spin-off Research Opportunities**
- **Co-authorship on Publications**
- **New Members allowed to Develop and Select One Project of Interest**

Industrial Membership Benefits

- Interactions with other companies focused on advancing photopolymerization in a non-competitive environment.
- Access to students with extensive experience in photopolymerization
  - ➔ *3M currently employs 5 Center Alumni and Affiliates*
  - ➔ *DSM Functional Materials employs 3 Center Alumni*
- CFAP Meetings at industrial and University locations
  - ➔ *Each member company can send multiple scientists and engineers*
  - ➔ *Spring 2012 Meeting at 3M*
    - Over 100 Scientists Attended
    - Industrial and Student Poster Session for Center Students and Affiliates
    - Mock Interviews and Feedback for Students
  - ➔ *Fall 2012 Meeting at University of Iowa*
  - ➔ *Spring 2013 (April 24-26) Meeting at DSM Functional Materials*

Industrial Membership

- Membership in the Center requires signing of a membership agreement and paying a membership fee
  - ➔ *Annual membership is $40,000*
  - ➔ *Can come from multiple divisions within a company (3M membership comes from 8 sources)*
- Members have the option of a royalty free, non-exclusive license to all IP for which a disclosure is filed while they are a member
- Current member companies 3M, Boeing, Avery Dennison, Henkel, DSM

Henkel

DSM
BRIGHT SCIENCE. BRIGHTER LIVING.

3M

BOEING®

AVERY DENNISON

Center Performance

- CFAP Started in 1999, Received NSF Funding in 2000, Graduated in 2006
- Currently, 5 Member Companies while 7 Research Projects are Funded - Highly Leveraged Funding
- Since 2000, more than 90 publications
- Since 2002, 12 CFAP Invention Disclosures, 3 Licensed to CFAP Companies
- Over 30 PhD students and post-doctoral researchers have worked on CFAP projects
- Multiple Spin-off Research and Other Interactions
- 2007 ACS Cooperative Research Award

Center Personnel

- CU: CN Bowman, KS Anseth, JW Stansbury, RL McLeod, C Musgrave
- UI: AB Scranton, C Coretsopolous, J Jessop, CA Guymon
- Established scientific record

  Since 1994:

  ➔ ***> 250 refereed publications on photopolymerization***

  ➔ ***> 50 patent disclosures***

- Complementary research expertise

  ➔ ***Free radical, cationic, donor-acceptor systems***

  ➔ ***Experimental and theoretical methods***

  ➔ ***Synthesis and Characterization, Scientists and Engineers***

  ➔ ***Emerging applications including nanotechnology and biomaterials***

- Established record of productive collaborations

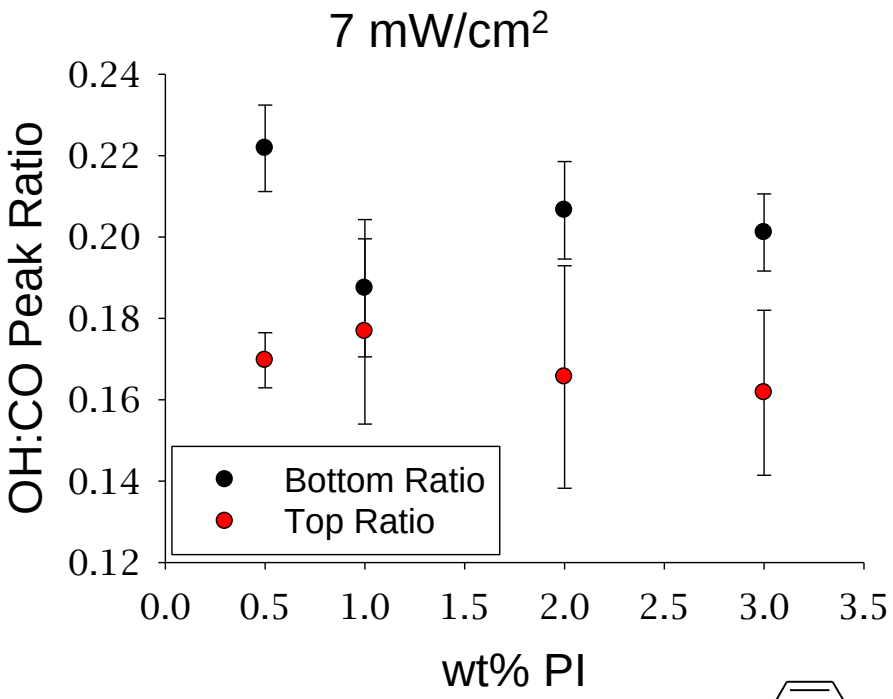
Current Research Projects

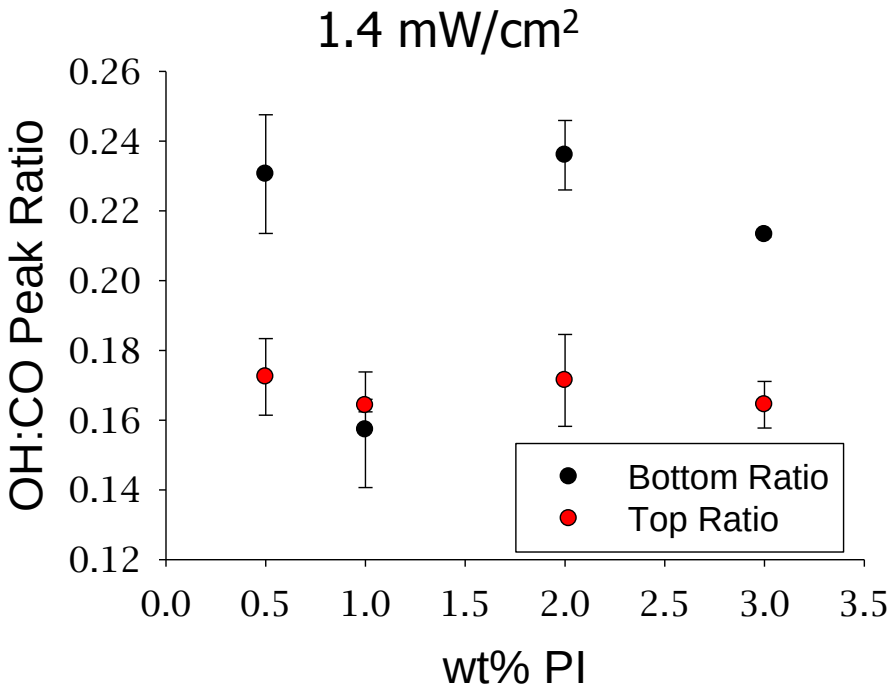
- **Multiple Mechanisms and Development of Novel Reactions**
  - ➔ ***Photo-Click Reactions***
- **Novel Characterization Techniques**
  - ➔ ***Property Evolution in Photopolymer Systems***
  - ➔ ***Dark Cure and Shadow Cure in Cationic Photopolymerization***
- **Novel Applications and Techniques**
  - ➔***Photo-enforced Stratification in Coating and Adhesive Materials***
  - ➔***Free Radical Photopolymerizations with LEDs***
- **Novel Materials Development**
  - ➔***Controlled Architecture and Functionality Photo-Curable Monomers***
  - ➔***Covalent Adaptable Networks***

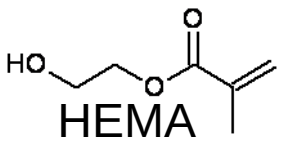
Completed Research Projects

- Methods to Reduce Oxygen Inhibition
- Fundamental Studies of Thiol/Ene Photopolymerizations
- Photoinitation Profiles in Thick Polymerization Systems
- Novel (Meth)acrylate Monomers for Ultra-rapid Photopolymerization
- Structural Evolution in Photocrosslinked Films
- Characterization of Crosslinked Degradable Networks
- Kinetic Studies of Hybrid Cationic/Radical Photopolymerizations
- Structured Illumination for Control of Polymerization Shrinkage Stresses
- Development of Parallel Evaluation Scheme for UV Monomer Formulations
- Photopolymerizable Clay Nanocomposites using Reactive Dispersants
- Molecular Fillers for Enhanced Polymer Mechanical Properties: Photopolymerized Molecularly-Filled Composites
- Measurement and Modeling of Oxygen Inhibition Layer in Radical Photopolymerization

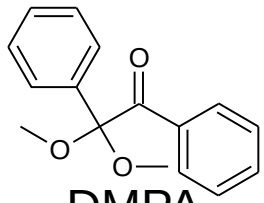
Photo-enforced Stratification - Monomethacrylate versus Diacrylate



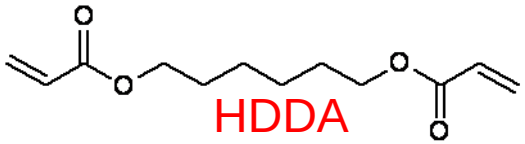




HEMA



DMPA



HDDA

- Up to 20 percent enrichment of HDDA at surface.
- Differences in mono vs di vinyl reactivity is a stronger driving for than reactivity ratios are for photo-enforced stratification.

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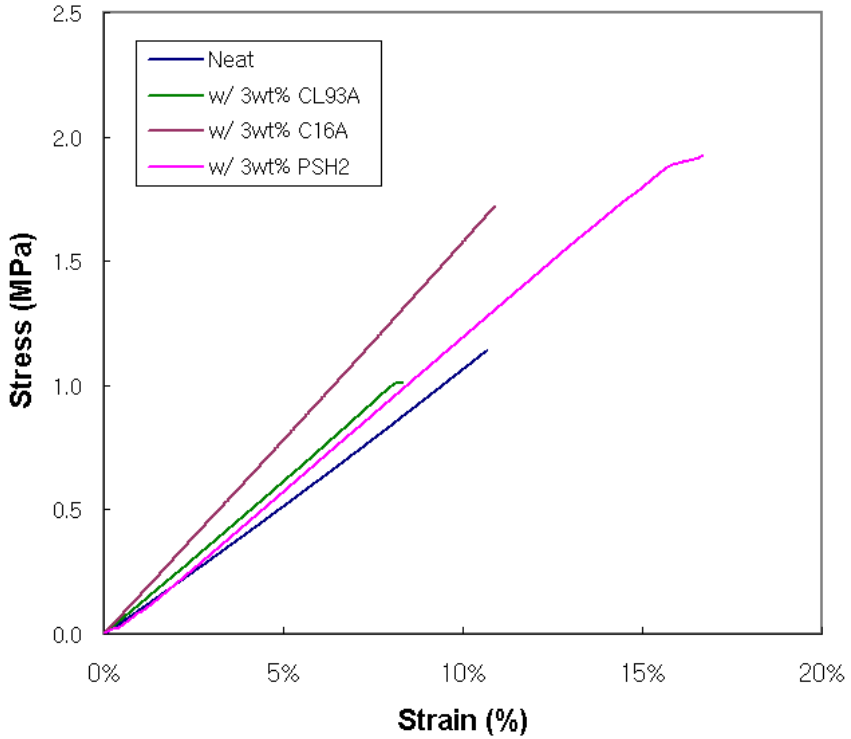
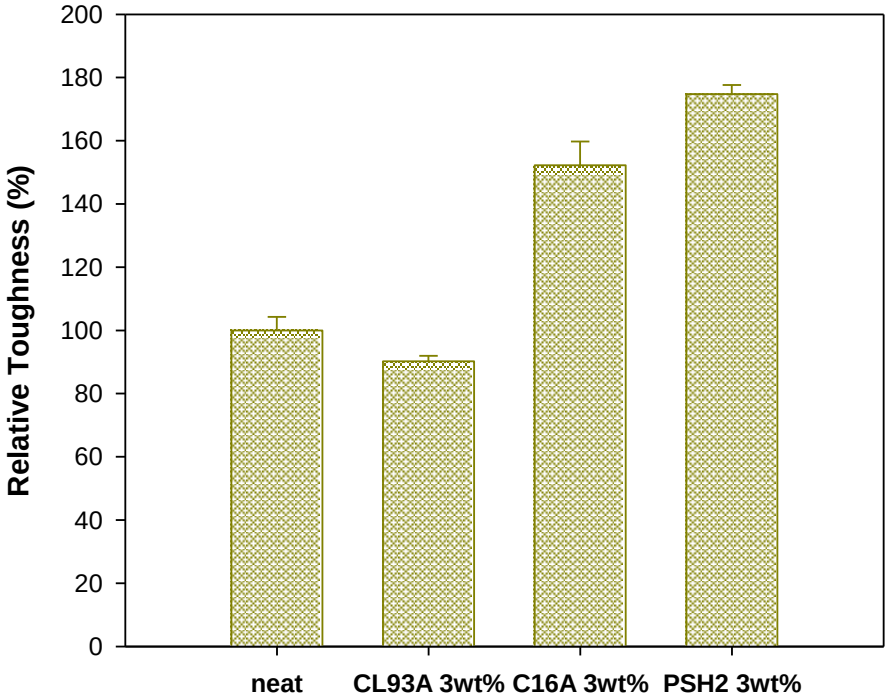
Photopolymerizations Center

Polymerizable Organoclays Increase Nanocomposite Toughness

CN9009/PEGDA/TrPGDA=30/30/40 wt ratio with 20mol% of TMPTMP





Acrylated organoclays increase the stiffness of nanocomposites, whereas thiolated organoclays mainly enhance the elongation.