High-Value Bioproducts

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Materials and the F-E-W Nexus

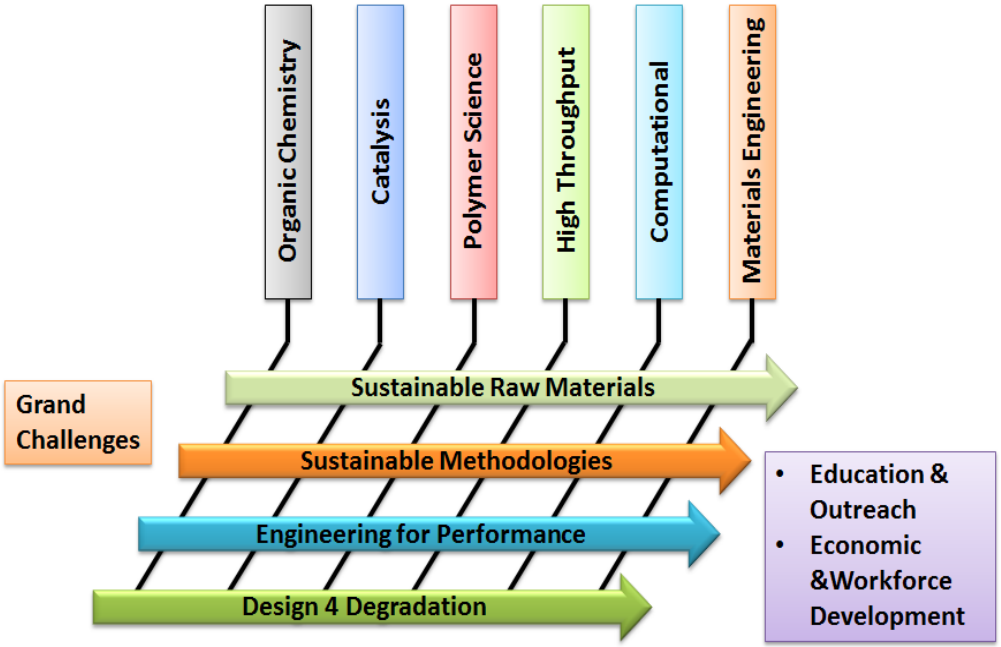
- Food
  - Packaging
  - Agricultural equipment
  - Timed-release fertilizers
  - Food additives
- Energy
  - Wire and cable insulation
  - Fracking fluids
  - Battery technology
  - Wind turbines
  - Photovoltaics
- Water
  - Anticorrosion coatings for pipelines, tanks
  - Membrane filtration systems

What are high value bioproducts?

- High Value
  - Utilization beyond use as a fuel
  - Use waste
- Bioproducts
  - Materials made from agricultural products
- To be successful
  - Meet or exceed properties of petrochemical materials
  - Cost effective

Center for Sustainable Materials Science

Objective: Provide a transformative approach to the development of sustainable materials derived from agricultural raw materials



Scientific Elements:

1. New Monomer Synthesis
2. Sustainable Methods
3. Polymers and Composites
4. Design 4 Degradation

Center Core-Researchers:

1. Prof. Dean Webster
2. Prof. Mukund Sibi
3. Prof. Sivaguru Jayaraman
4. Prof. Chad Ulven
5. Prof. Bret Chishlom
6. Prof. Qualani Chu
7. Prof. Guodong Du
8. Prof. Alex Parent

Opportunities: (1) collaborative projects; (2) Research experiences for undergraduates; (3) Graduate assistantship program
(4) Seed grants for PUIs / TC investigators as a collaborative effort

ND EPSCoR
Advancing Science Excellence in North Dakota
Experimental Program to Stimulate Competitive Research

www.csms-ndsu.org

DakotaBioCon

Dakota Bioprocessing Consortium

Vision: Become the intellectual leader for lignin bioprocessing.

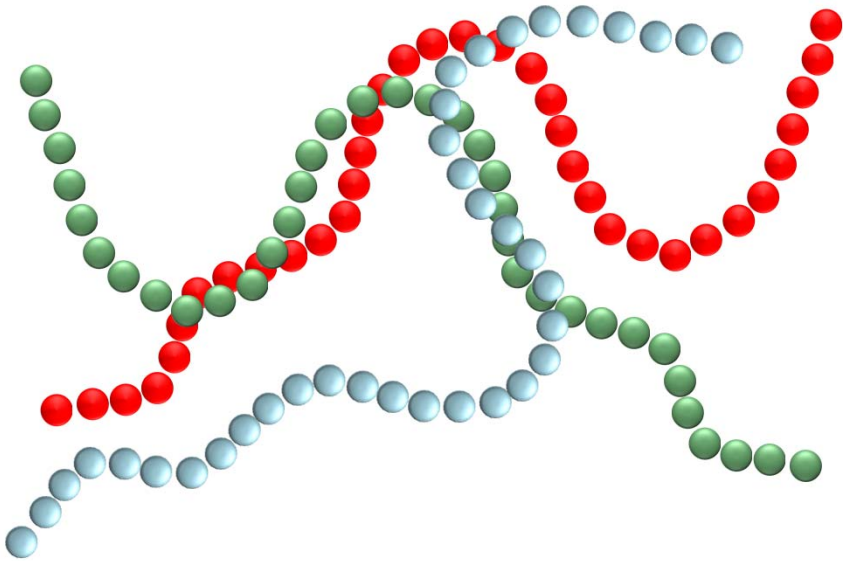
North Dakota State University
University of North Dakota

South Dakota State University
South Dakota School of Mines

Lignin → Bioprocessing → Separations → Chemicals → Polymers

Dakota BioCon

Thermoplastics



Thermoset Polymer Applications



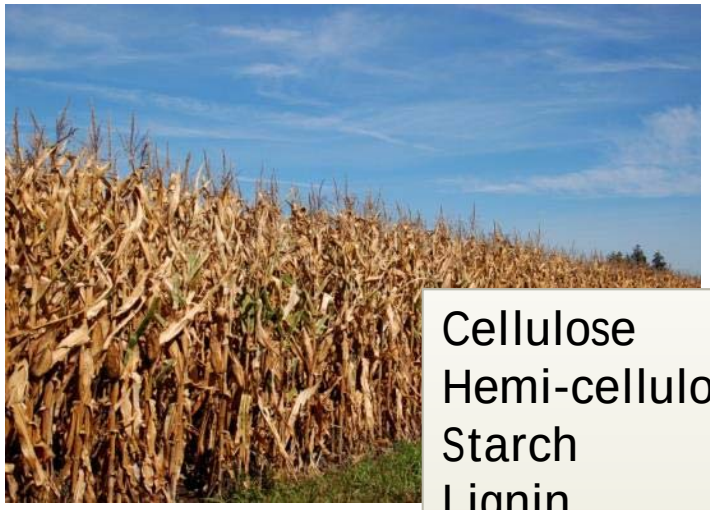








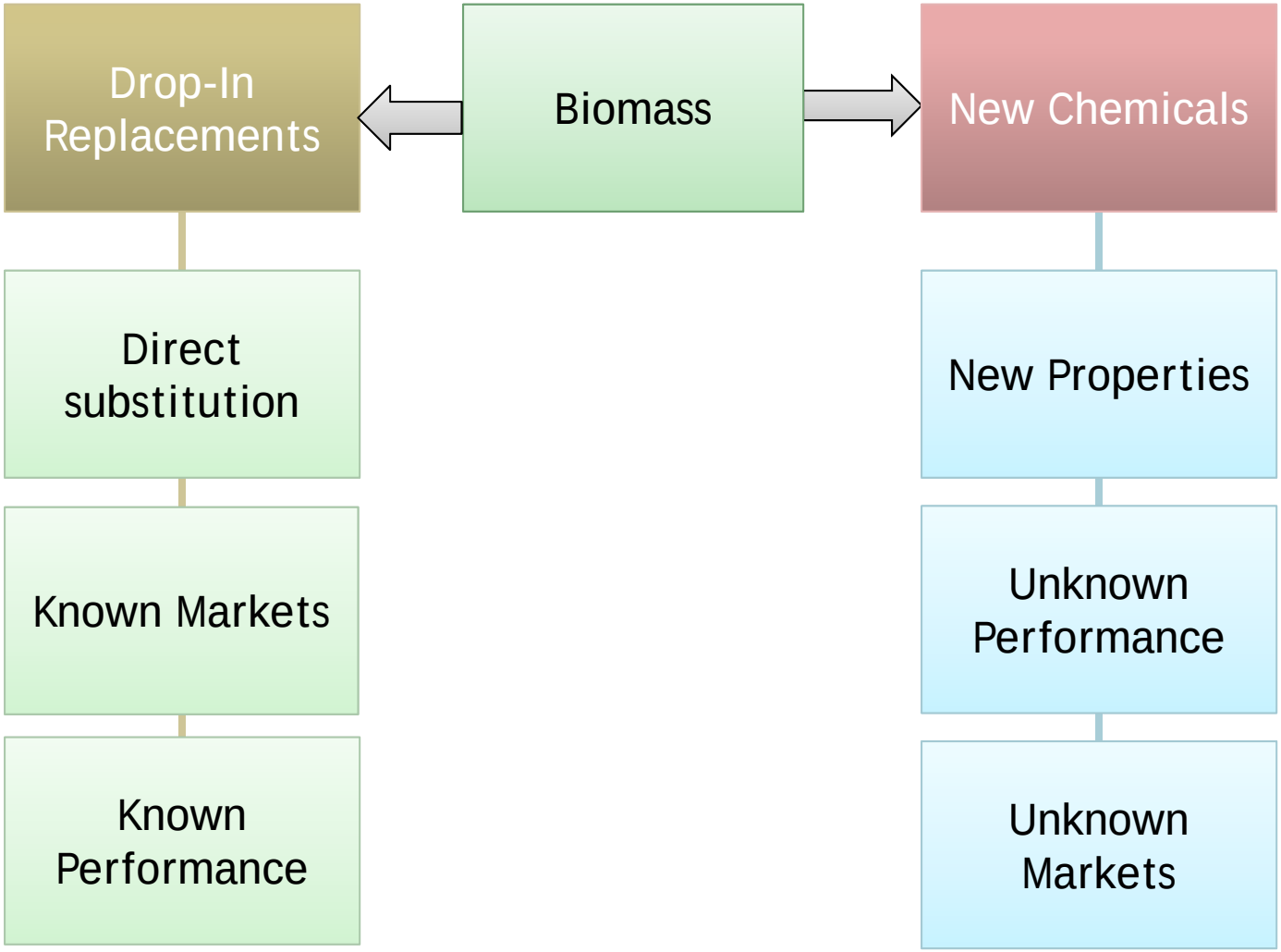

Agricultural Sources of Chemicals



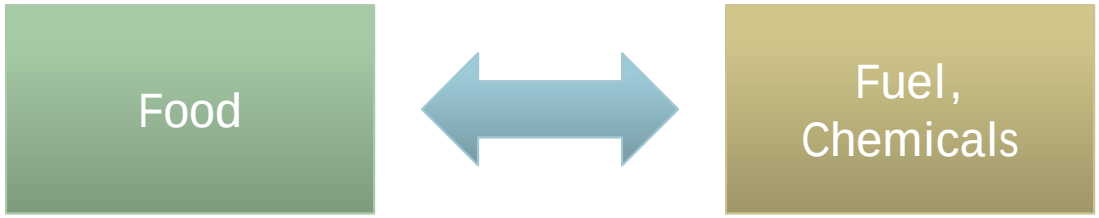
Cellulose
Hemi-cellulose
Starch
Lignin
Rosin
Tall Oil FA
Terpenes

Drying Oils
Semi-Drying Oils
Glycerol
Fatty Acids

Chemicals from Biomass

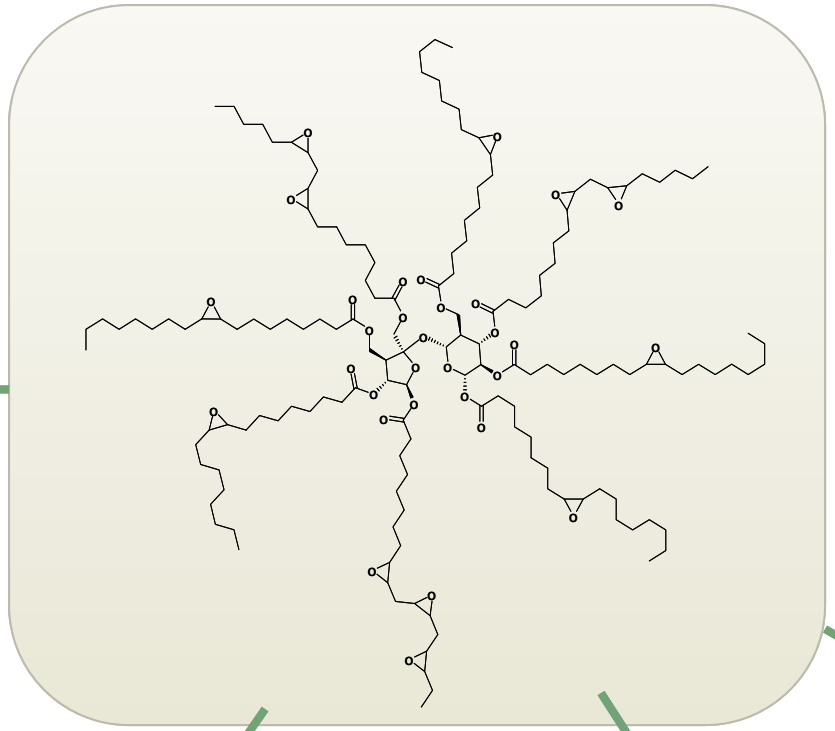


Some Important Issues



- Supply chain
- Funding
- Non-food crops
- Non-food parts of crops

ESE Resins: A Platform Technology



Polyols

Crosslinking

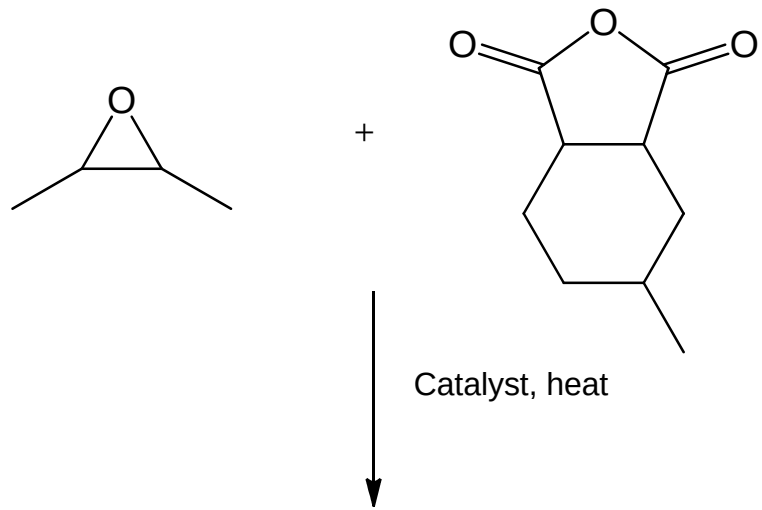
Photo-polymerization

(Meth)acrylates

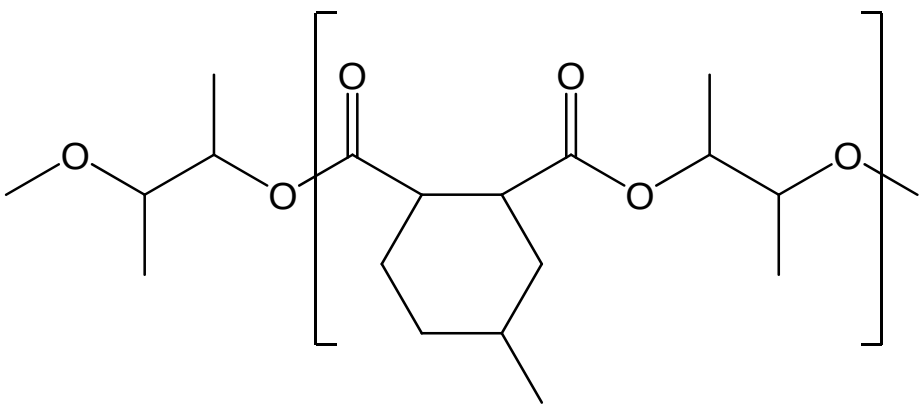
Thermal Crosslinking - Blocked Acids

Thermal Crosslinking - Anhydrides

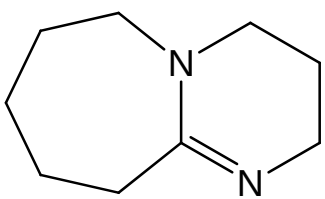
Anhydride Curing



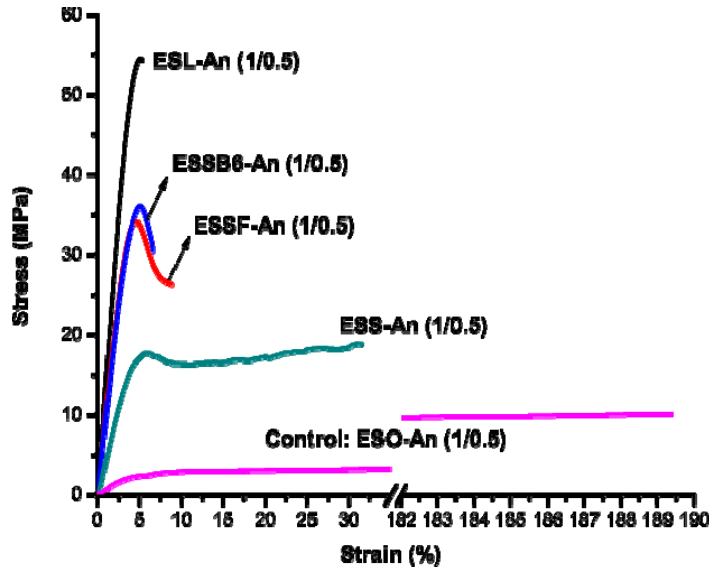
- Strong base, metal catalysts
- Thermally activated
- Forms a polyester
- Some polyetherification



Initial studies:
Curing: 80°C, 12 Hrs
Catalyst: DBU



Tensile Properties



Epoxy compound	*Modulus (MPa)*	*Tensile strength (MPa)*	*Elongation at break (%)*	*Tensile toughness (J) X 10^3*
ESL	1395 ± 191	45.8 ± 5.4	5.7 ± 2.6	8.44 ± 3.5
ESSF	909 ± 179	31.5 ± 3.2	8.5 ± 2.7	11.5 ± 6.3
ESS	497 ± 38	20.3 ± 4.3	21.7 ± 7.8	29.4 ± 9.2
ESSB6	1002 ± 52	35.1 ± 3.6	5.4 ± 0.7	9.1 ± 3.8
ESO (Control)	65 ± 10	10.2 ± 2.5	167 ± 19	97 ± 13.8

Remarkable tensile modulus for a VO based system

Pan, Sengupta, Webster, *Biomacromolecules*, 2011, 12, 2416-2428.

Composites with Natural Fibers

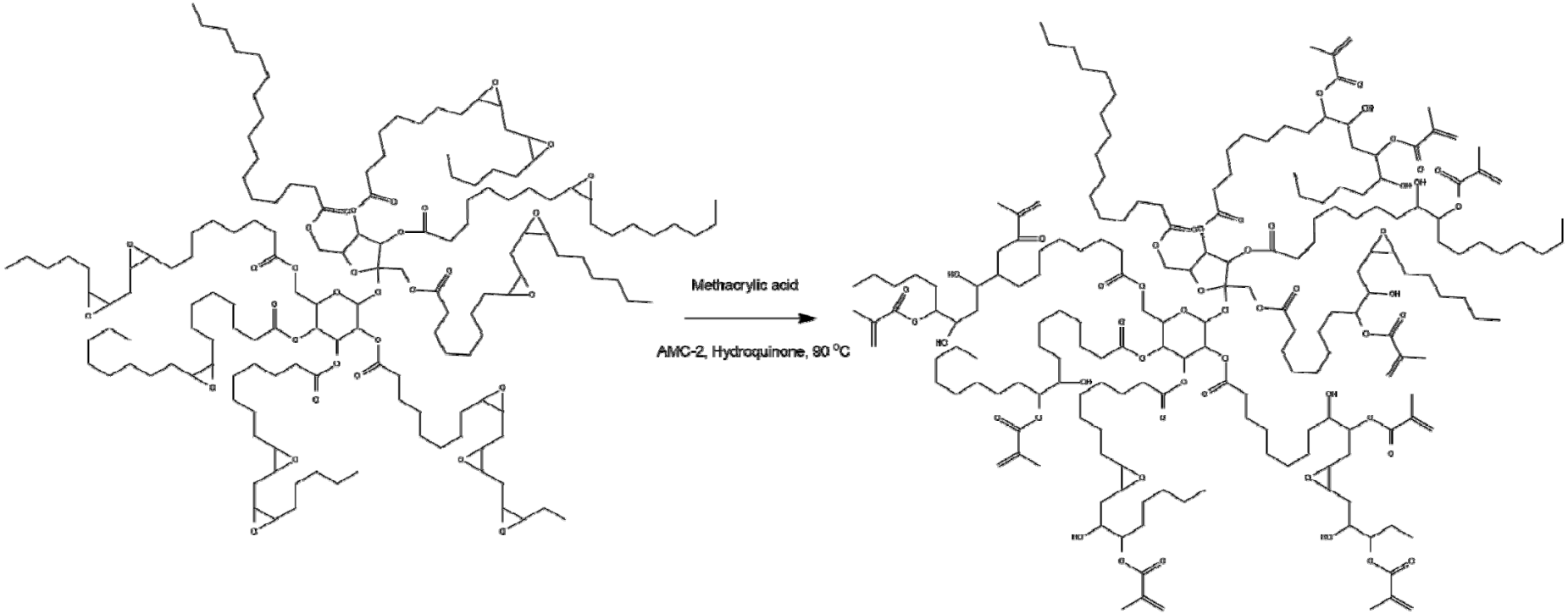
Biobased resin gives equivalent or better performance than petrochemical resin

Reinforcement: Loose flax fibers

	Untreated Fiber			NaOH Treated Fiber	
Category	Araldite	ESS F1	ESS F2	Araldite	ESS F2
Tens. Str. MPa	158.09 ± 21.69	154.16 ± 6.77	152.58 ± 15.99	NA	178.31 ± 38.93
Flex. Str. MPa	195.65 ± 24.64	252.42 ± 24.20	340.30 ± 28.17	242.00 ± 22.5	259.45 ± 12.36
Sht. Beam Str. MPa	12.65 ± 1.56	22.32 ± 3.16	25.63 ± 2.46	23.32 ± 0.25	25.35 ± 1.76

Data courtesy of C. Taylor, T. Krosbakken, Chad Ulven, NDSU Mechanical Engineering

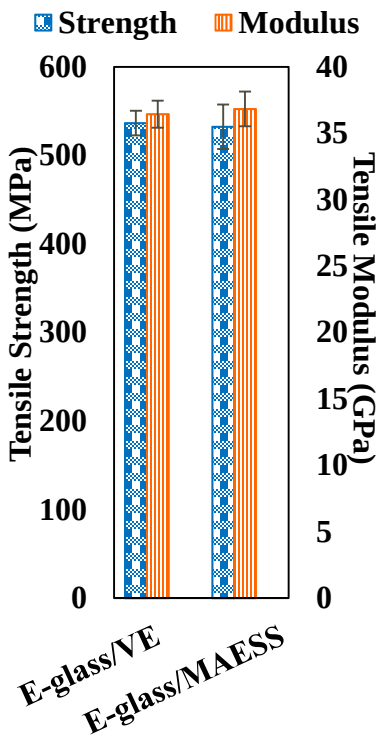
Methacrylated ESS for Composites

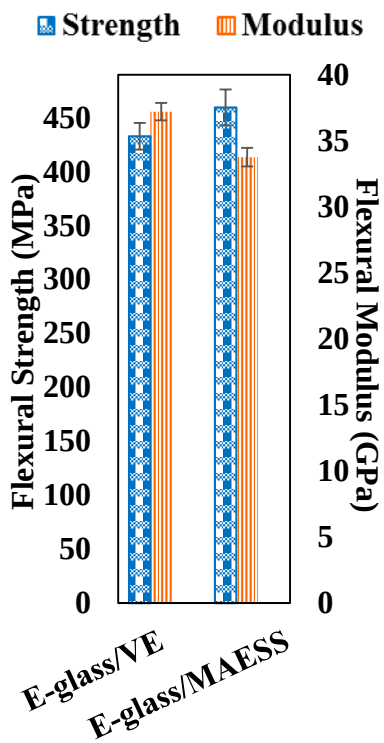


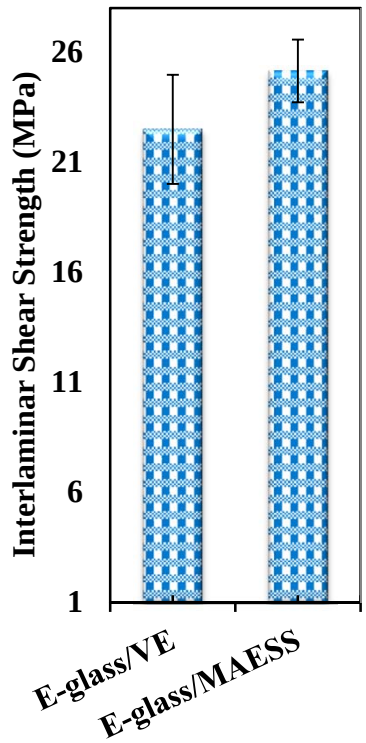
Cure Catalysts: Luperox P, Luperox 10M75
Cure Schedule:
150 °C for 1 hour, 175 °C for 1 hour, and 200 °C for five hours

Glass Fiber Composites

MESS Resin System Comparable or Better Than Vinyl Ester (VE)







Data from: Nassibeh Hosseini, Chad Ulven, NDSU Mechanical Engineering

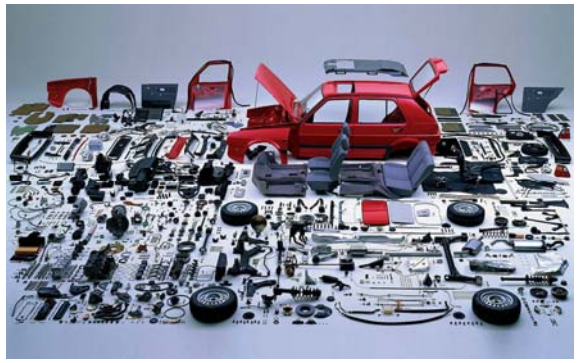
Plastic Waste

This is *not* the solution

Concept: Product Dissassembly

Car,
Device, etc.

Dissassembly



Metal

Metal

Metal

Chemical

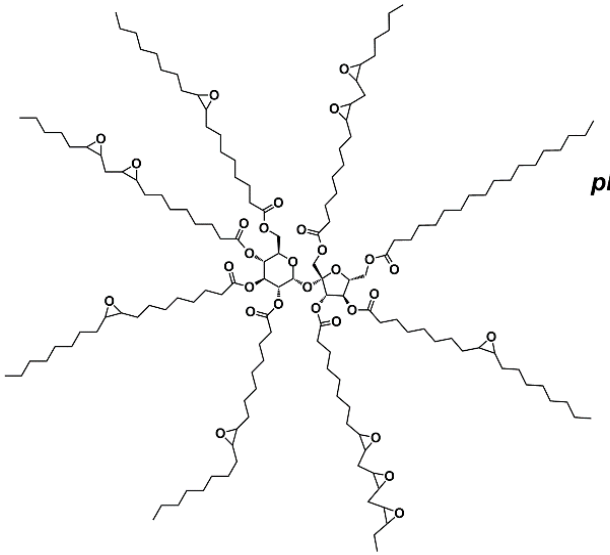
Chemical

Chemical

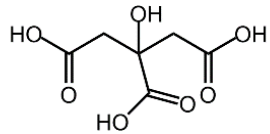
Reuse

Polymers can play an important role in this concept

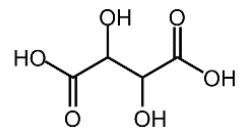
Bio-based, zero VOC, degradable thermoset



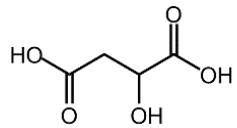
Epoxidized sucrose soyate (ESS)



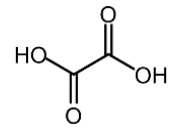
Citric acid
pK_{a1}=3.13, pK_{a2}=4.76, pK_{a3}=6.39



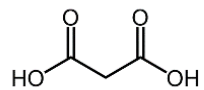
Tartaric acid
pK_{a1}=2.98, pK_{a2}=4.34



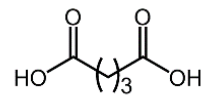
Malic acid
pK_{a1}=3.40, pK_{a2}=5.11



Oxalic acid
pK_{a1}=1.25, pK_{a2}=4.14



Malonic acid
pK_{a1}=2.83, pK_{a2}=5.69

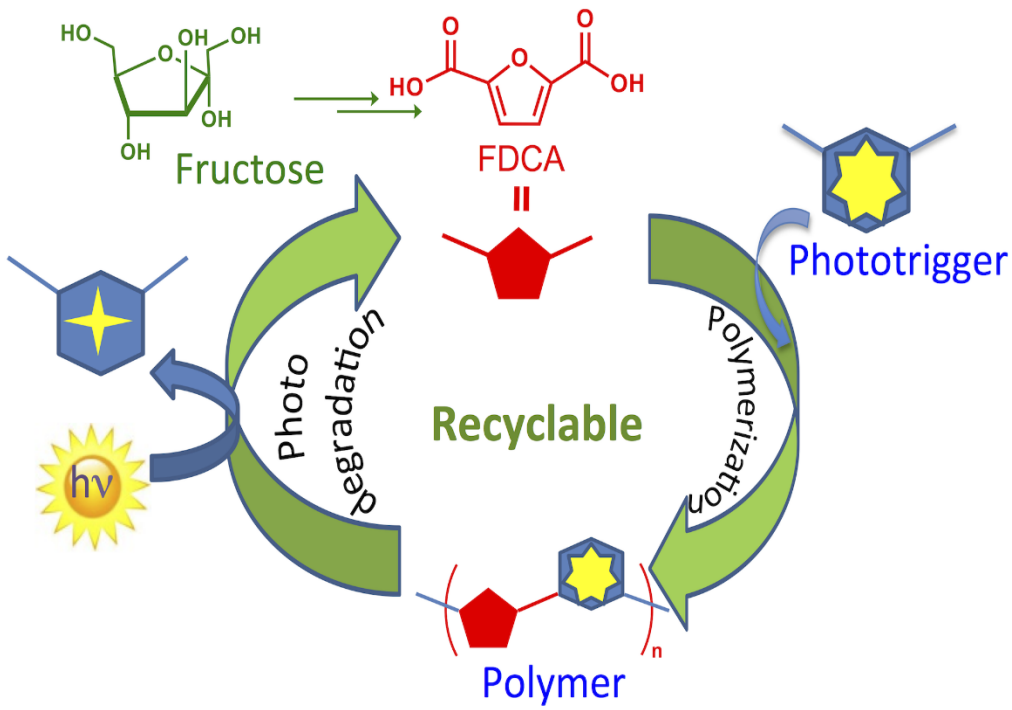


Glutaric acid
pK_{a1}=4.34, pK_{a2}=5.22

- Excellent physical and mechanical properties
  - Hardness, flexibility, adhesion, etc.
- Degradable using base (NaOH)

Macromolecules, **2015**, *48* , 7127–7137

Proof of Concept



Saravanakumar Rajendran, Ramya Raghunathan, Ivan Hevus, Retheesh Krishnan, Angel Ugrinov, Mukund P. Sibi, Dean C. Webster and J. Sivaguru, *Angew. Chem. Int. Ed.*, **2015**, 54, 1159-1163.

Summary

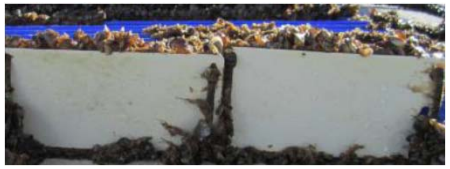
- Renewables can be used to create new types of polymers
- High functionality resins can be derived from sucrose esters of vegetable oils
- High functionality leads to high crosslink density in thermosets
  - High modulus
  - High hardness
  - Good solvent resistance
- Properties are comparable to petrochemical counterparts
- It is possible to design polymers for their eventual degradation

Parker Dam - Arizona

Bureau of Reclamation, U.S. Department of the Interior

Previous Coatings Set

A4-10 and A4-20 after 12 mos



C4-10 and C4-20 after 12 mos

C4-10 after 24 mos

C4-20 after 24 mos

New Coatings Set

A4-20 after 16 weeks

C4-20 after 16 weeks

SO-PM0021 after 16 weeks

SO-PM0025 after 16 weeks

Coatings can prevent the settlement of mussels in waterways

Thank You!