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Department of Chemical and Biological Engineering

Waterborne Glycerol Based Thermoplastic Adhesives for Wood Composites

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United States Department of Agriculture
National Institute of Food and Agriculture

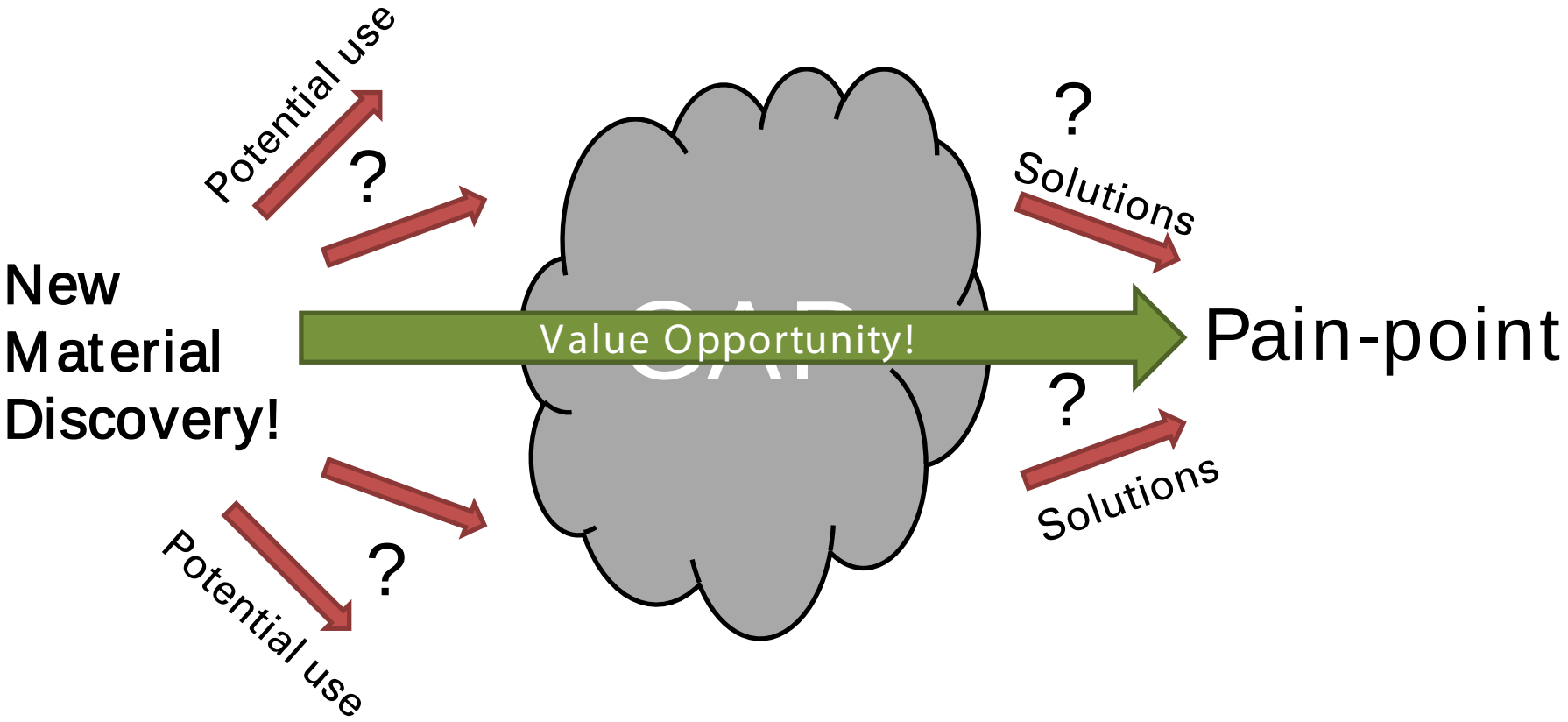
ARGO GENESIS CHEMICAL LLC

Thanks to…

- USDA
- Adventus
- Joe Marcinko at Polymer Synergies
- Argo Genesis Chemical LLC
- Seneca Petroleum
- Cochran research group



The first problem with technology translation



Bringing new biopolymers to market



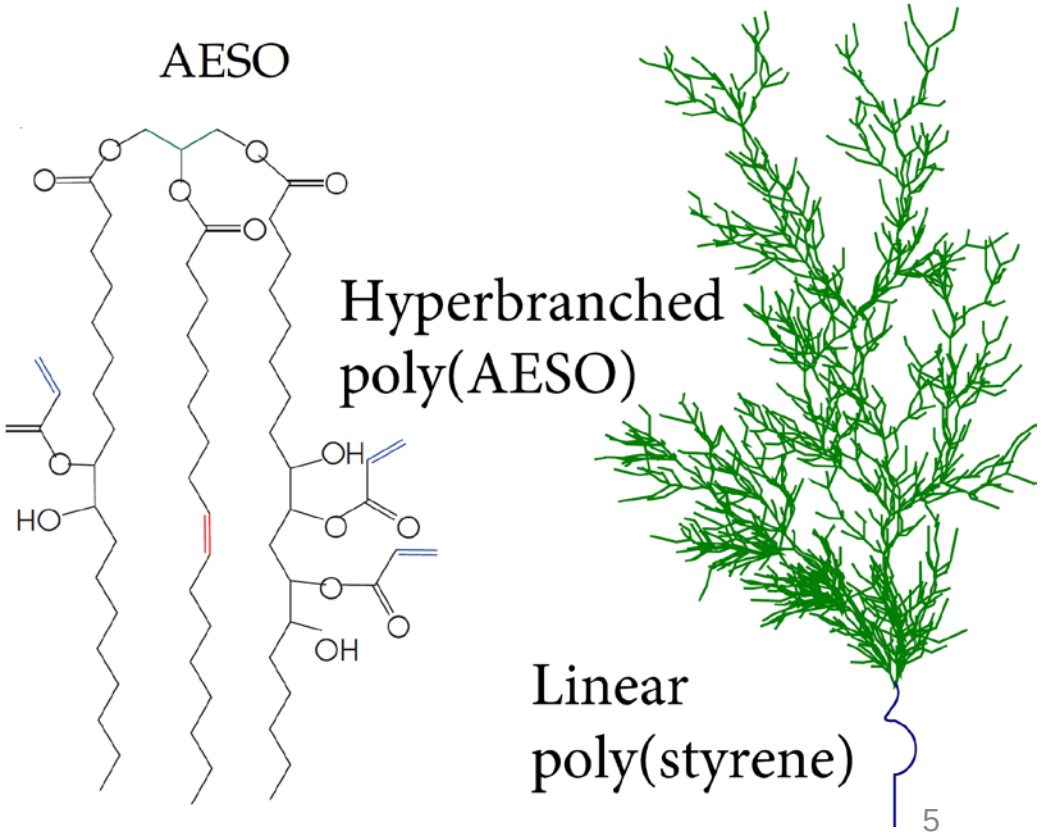


$15M licensee investment in partnership with ISU in this and related technologies.

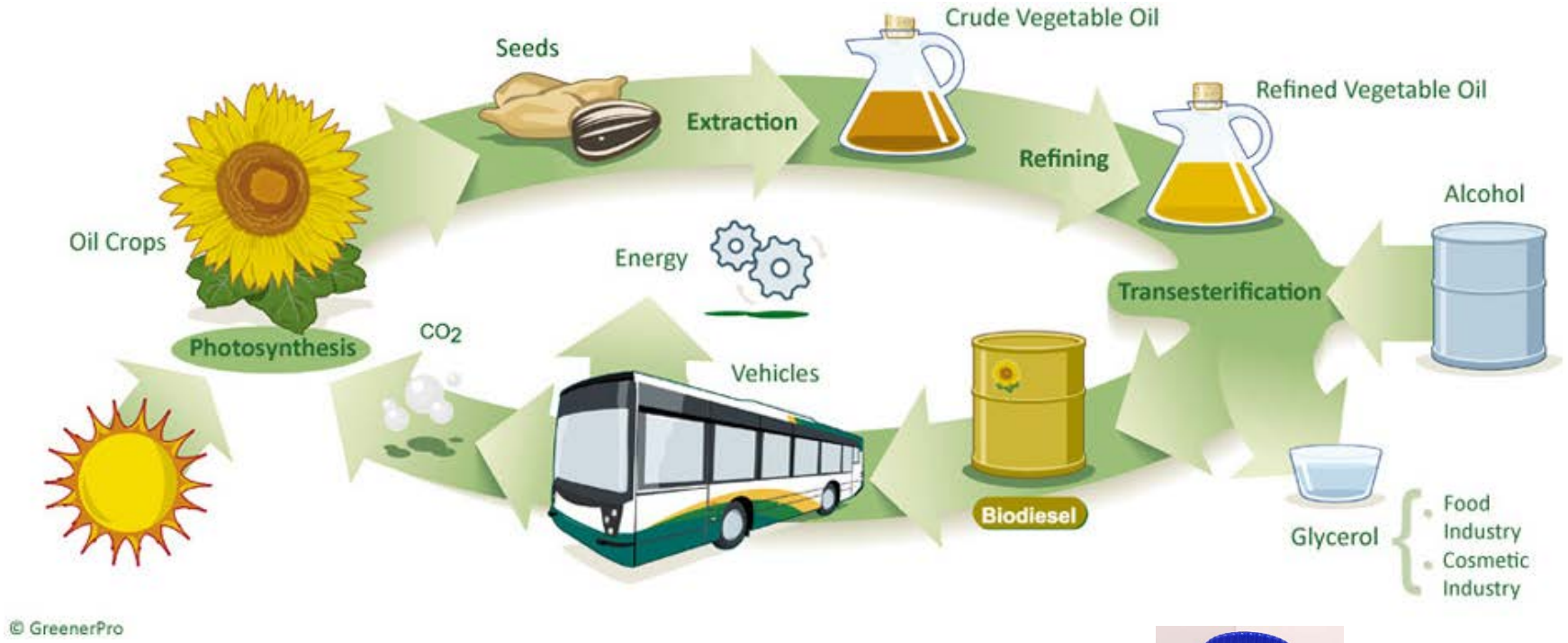
Success with other polymers

- AESO –Acrylated Soybean Oil
  - Multifunctional monomer that can be used as a precursor to thermoplastics



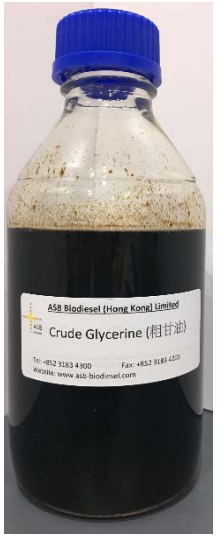


Soybean oil to Biodiesel

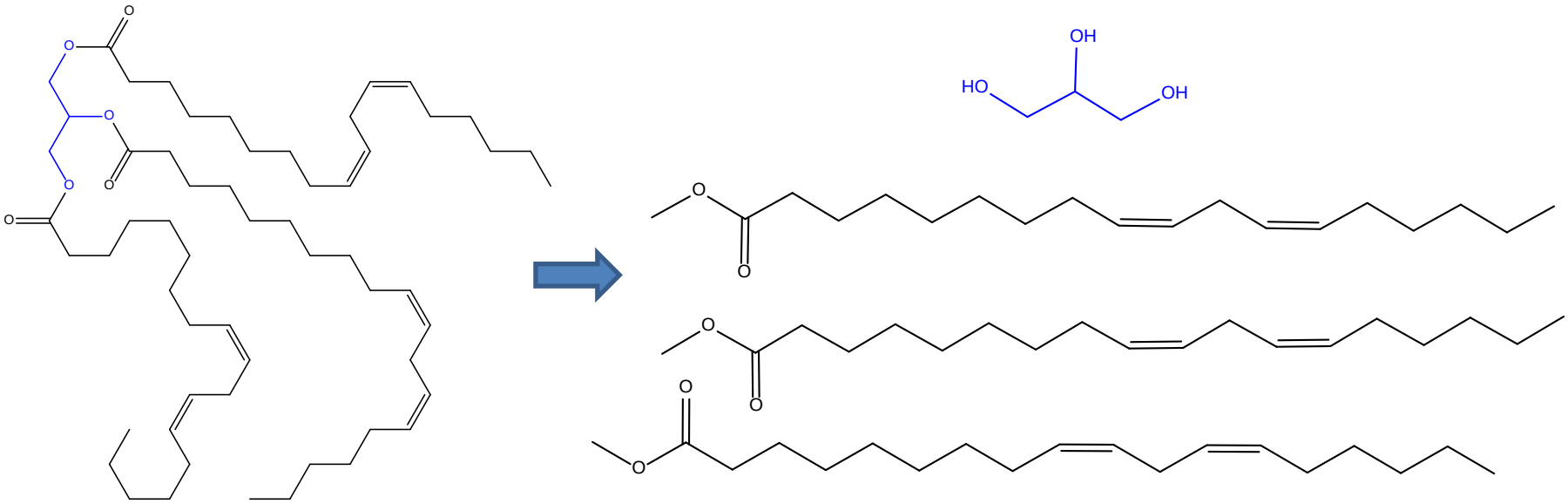


Crude Glycerin

- ≈ $0.10 / lb FOB
- Small biodiesel producers are unable to refine it
- ≈ 80% glycerine, 15 % H_2O, 5% MeOH
- Contains Ash, Soaps, FAMES, FFAs, MONG

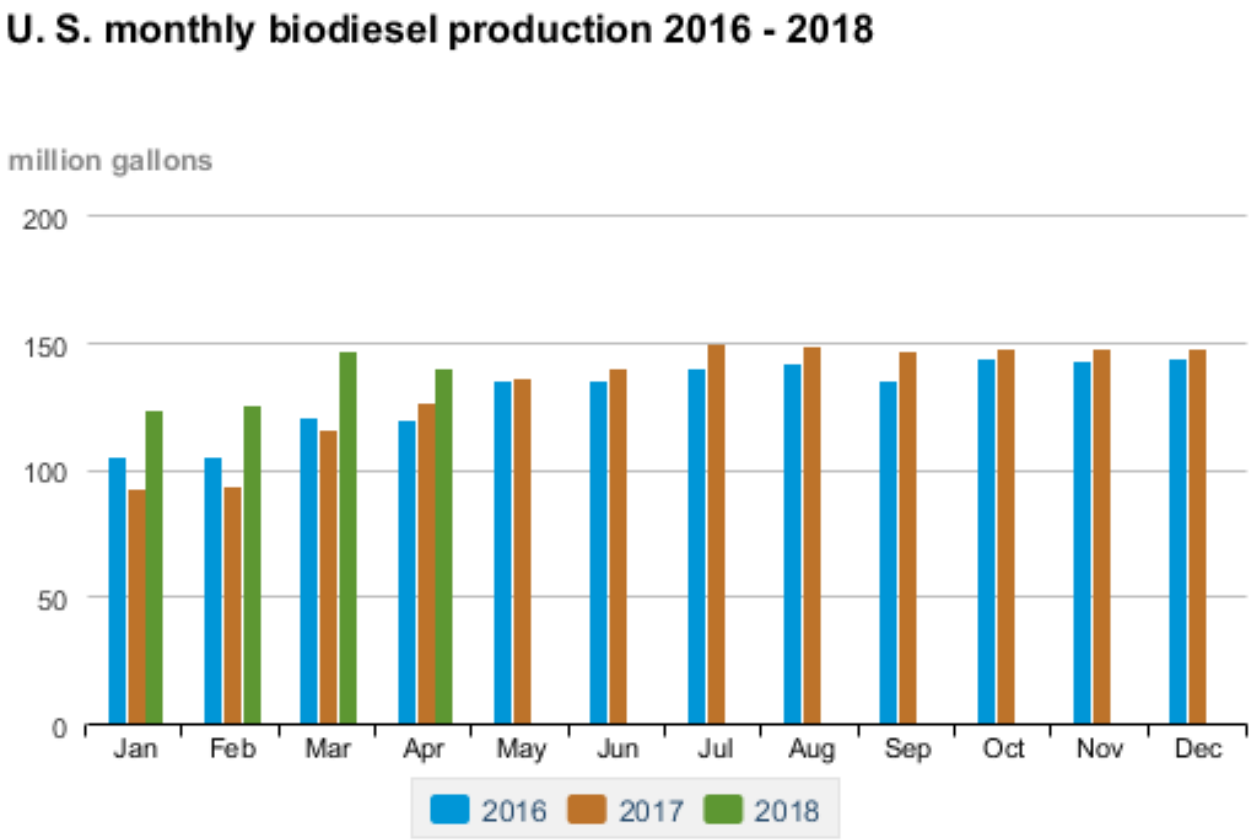


Soybean oil to Biodiesel



- Generates 10% glycerol w/w as waste

Glycerol Glut

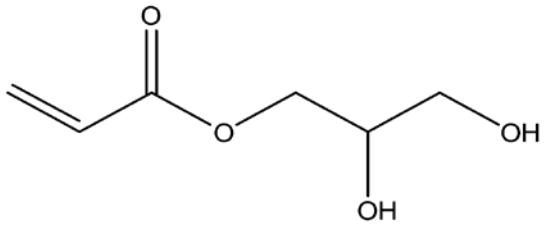


U.S. Energy Information Administration, Form EIA-22M Biodiesel Monthly Survey.

150 million gallons of biodiesel
=
50 thousand metric tons of glycerol per month

Acrylated Glycerol (AG)

- Precursors are cheap & bountiful
- Straightforward synthesis via (trans)esterification
- Should produce a water soluble polymer
- Should have wide solvent compatibility

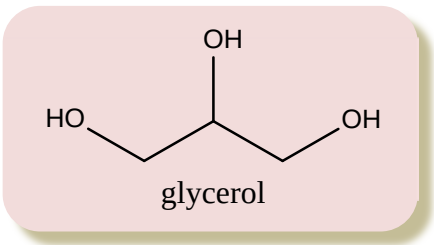


1-glycerol acrylate

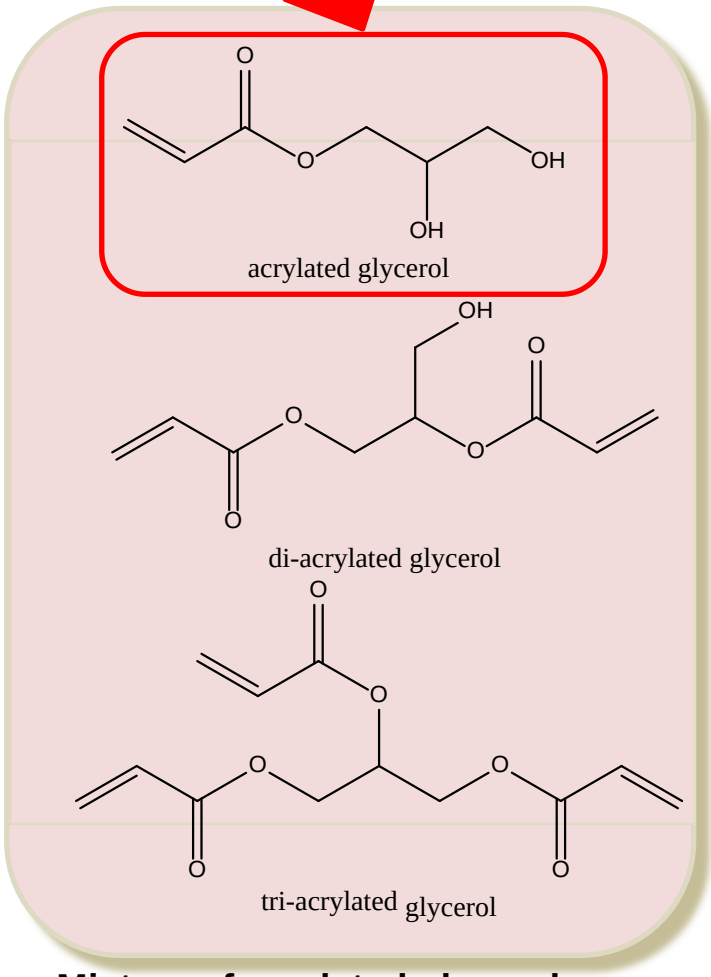
Raw Material Components & Processing	Cost/lb	Percentage of Formulation
Glycerol	$0.20	56%
Acrylic Acid (contract pricing)	$0.40	44%
AG	$0.28	

Main Material of interest

Difficult (costly) to make *solely* monofunctional acrylates



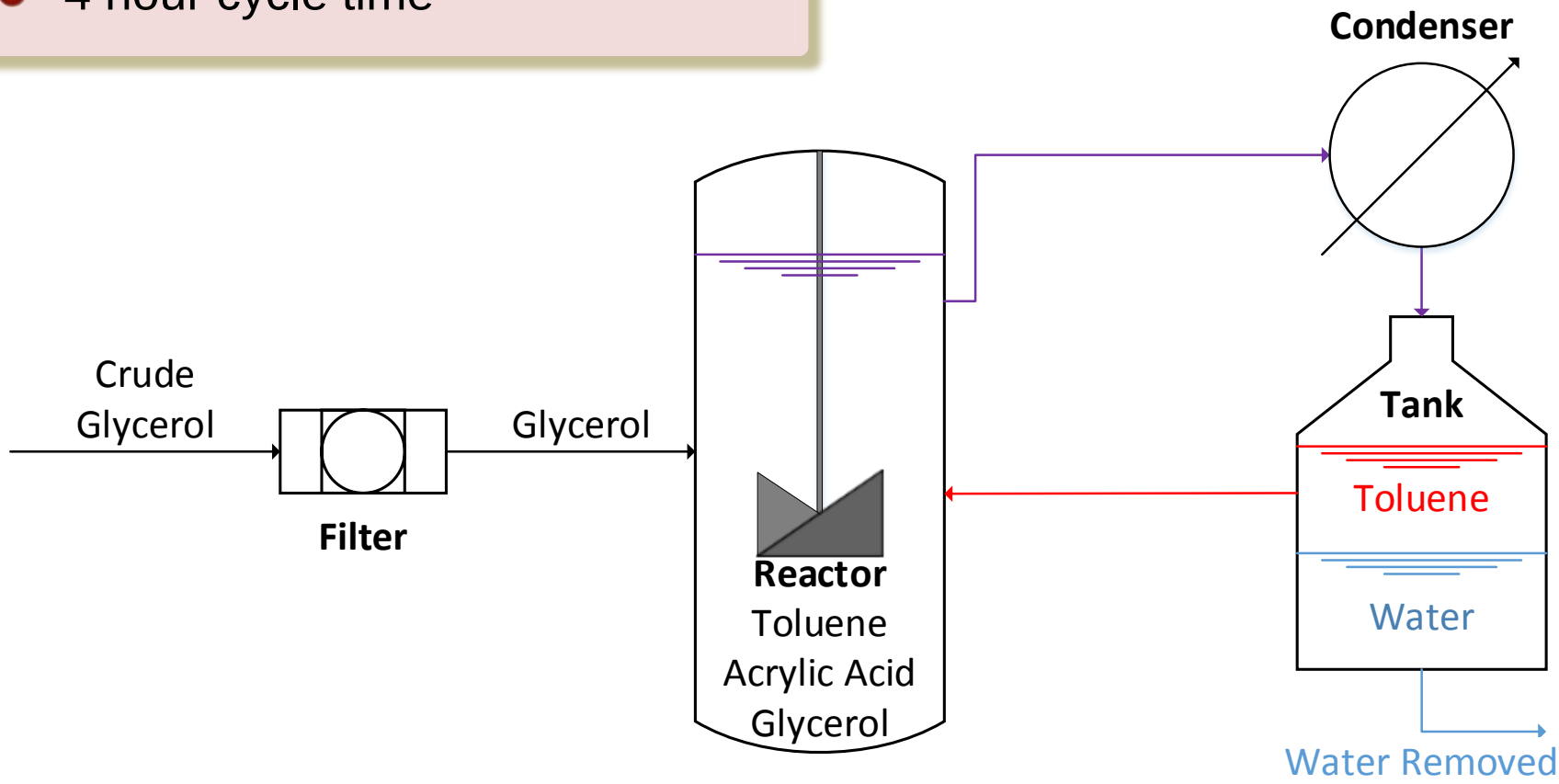
Mixture results from easier (economical) esterification processes



Mixture of acrylated glycerols

Upgrading Crude Glycerine

- 110 ^{o}C, atmospheric pressure
- 4 hour cycle time

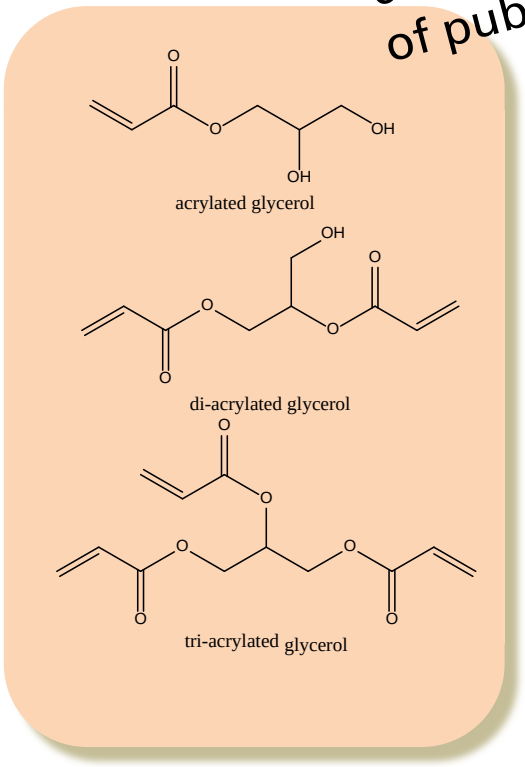


Polymerization Expectations vs Reality

Thermoset

Expectation of polymer chemistry community as documented by 100s of publications on the topic





Mixture of acrylated glycerols

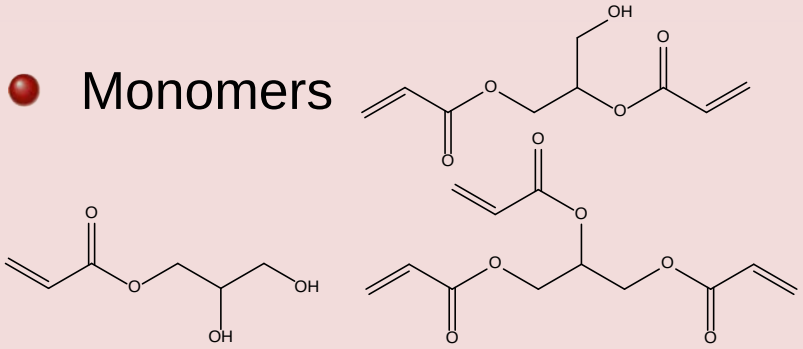
RAFT Polymerizatic

Thermoplastic rubber

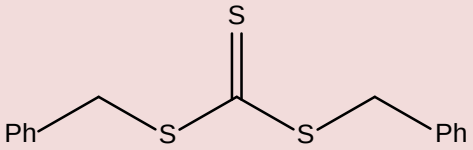


RAFT Polymerization

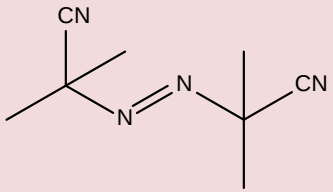
- Monomers



- Dibenzyl-carbonotrithioate (CTA)



- Initiator (AIBN)



- Solvent (Water or MeOH)



What next?





Potential use ?

al

ery!

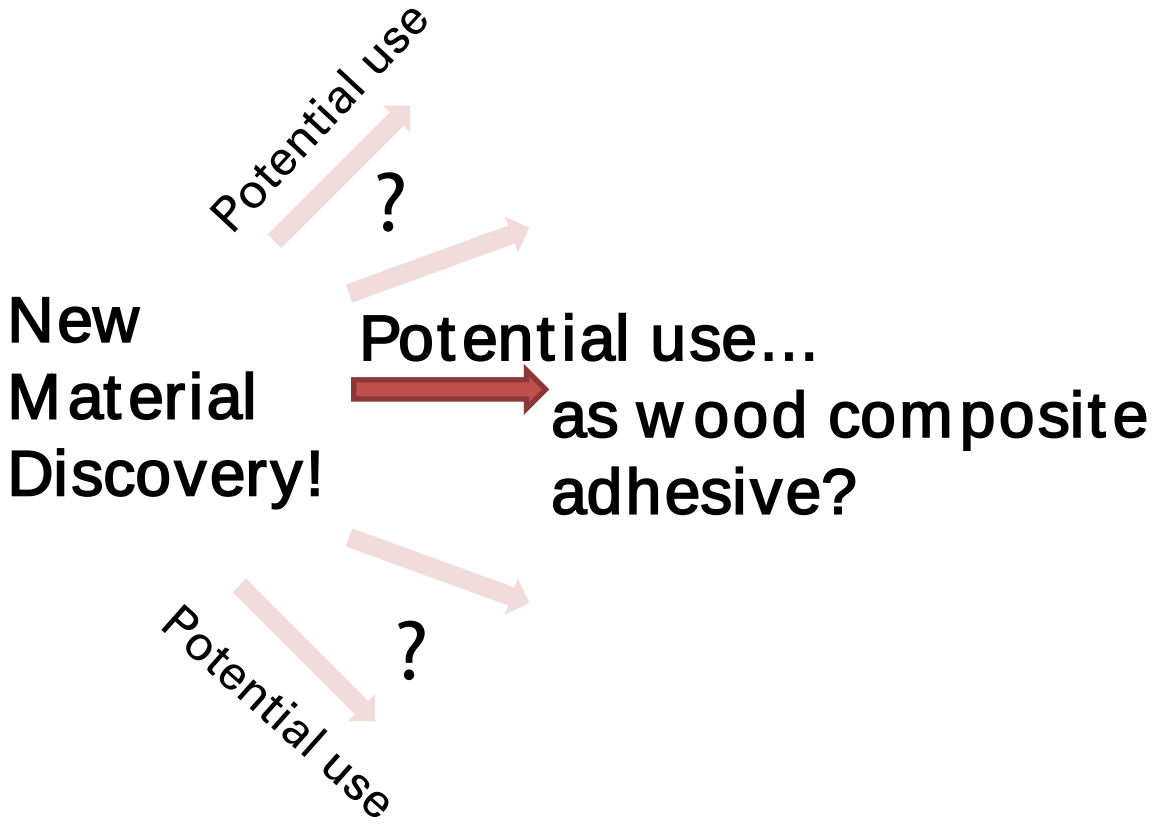
tential use ?

- Low T_g (≈ -45 °C),
  - could be a rubber
- Molecular weight up to 10 MDa
- -OH functionality
  - H_2O solubility
  - Further chemistry?
- Residual acrylic
  - Curable ?
- Sticky when even slightly wet
  - Adhesives?

14/717,777: Poly(Acrylated Polyol) and Method For Making and Using Thereof as Asphalt Rubber Modifiers, Fracking Additives or Fracking Fluids

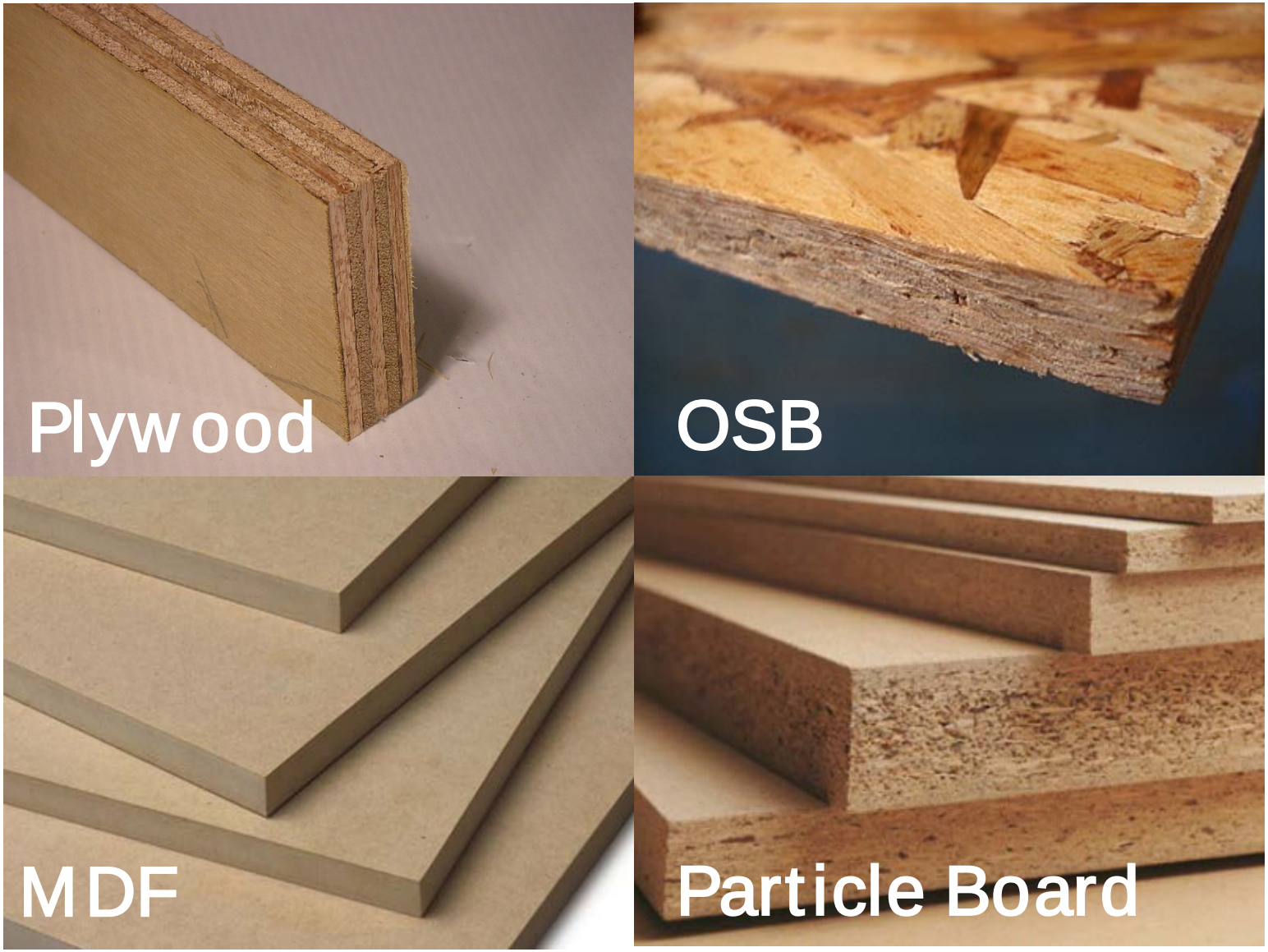
What next?





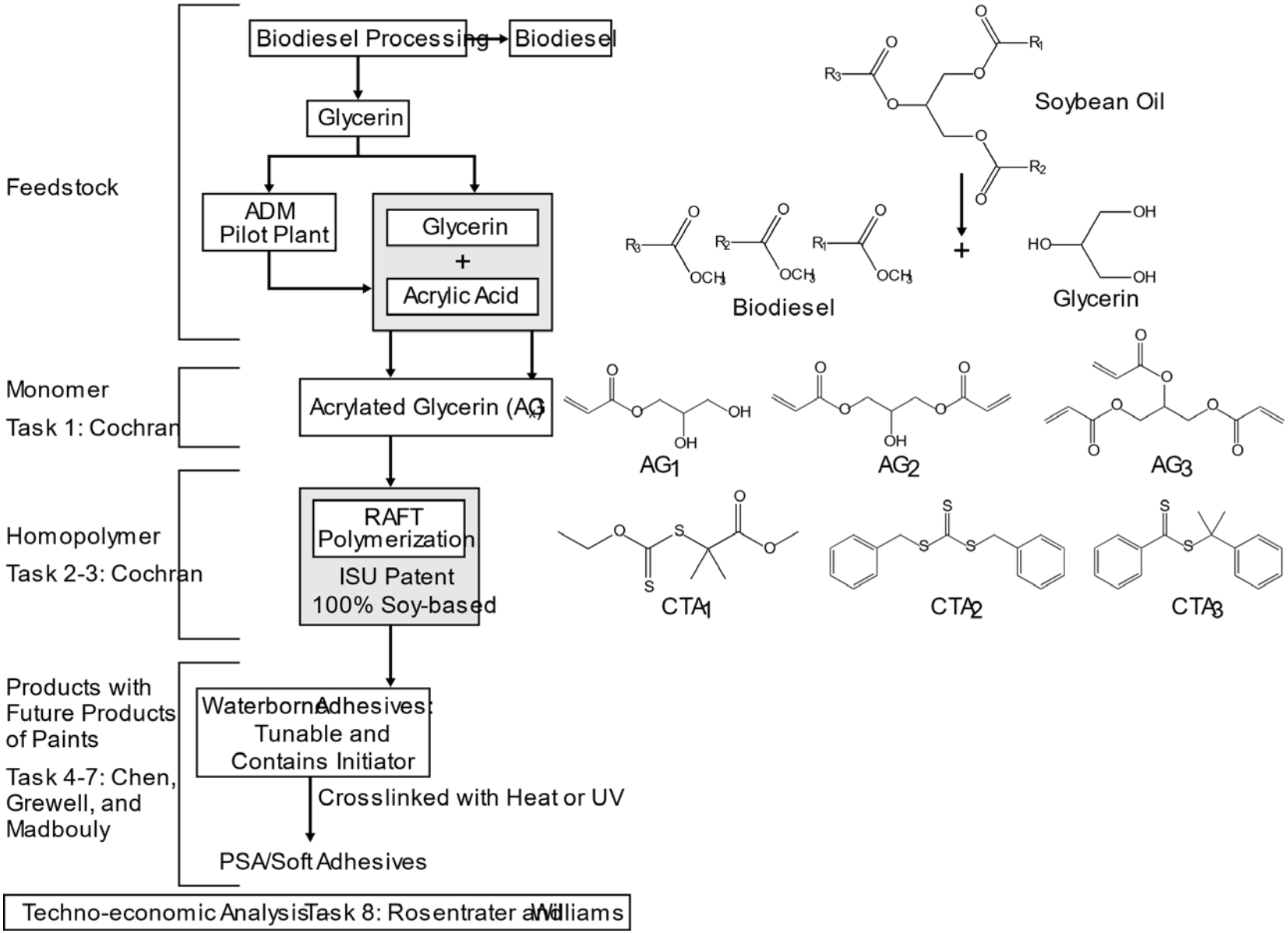
14/717,777: Poly(Acrylated Polyol) and Method For Making and Using Thereof as Asphalt Rubber Modifiers, Fracking Additives or Fracking Fluids

Wood Composites



2014 USDA Critical Agricultural Materials:

Specifically requested VOC-free adhesives produced from biofuels for wood composites

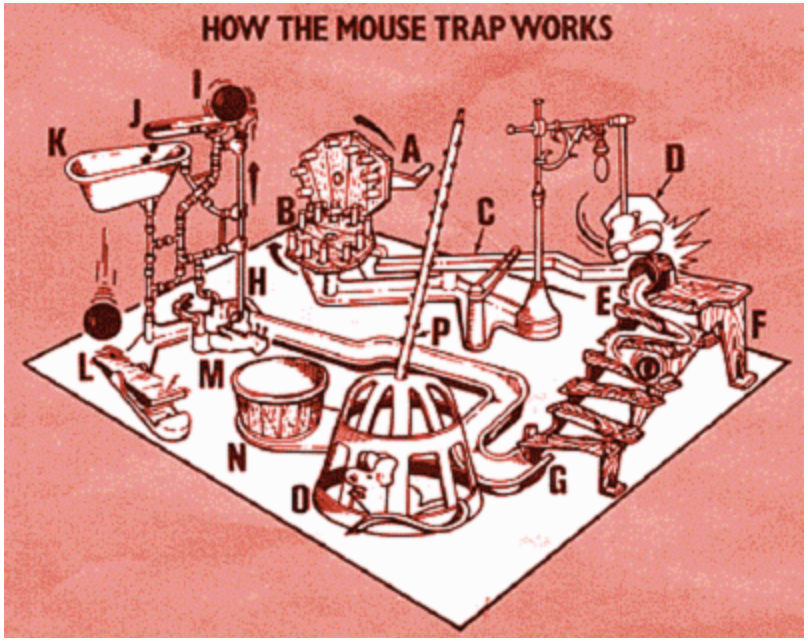


New Material Adoption

"*As Good As*" is not enough

- No one wants to use something new to solve a problem that has already been solved

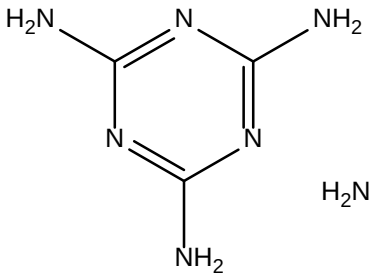




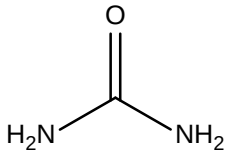
- "Better" – must meet performance specs
- "Cheaper"
- "Other" - Another benefit

What's the competition look like?

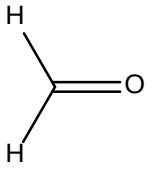
- Formaldehyde based
  - Urea Formaldehyde (UF)
  - Phenol Formaldehyde (PF)
  - Melamine Formadehyde (MF)



melamine



urea

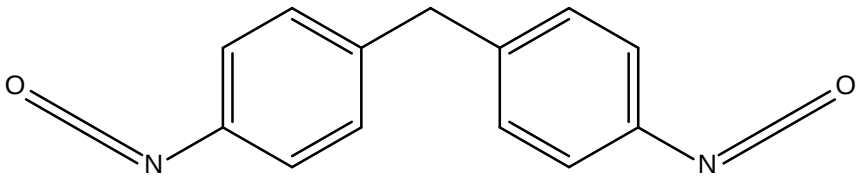


formaldehyde

These are cheap resins ($0.14 – $0.55/lb)

- Urethane based

  Methylene Diphenyl Diisocyanate (MDI)
  - High water resistance
  - Excellent strength
  - Formaldehyde free
  - Low green tack
  - Moderate cost ($1.00/lb)



MDI

Lumber Market & Adhesive Use (3/4” Board Equivalent)

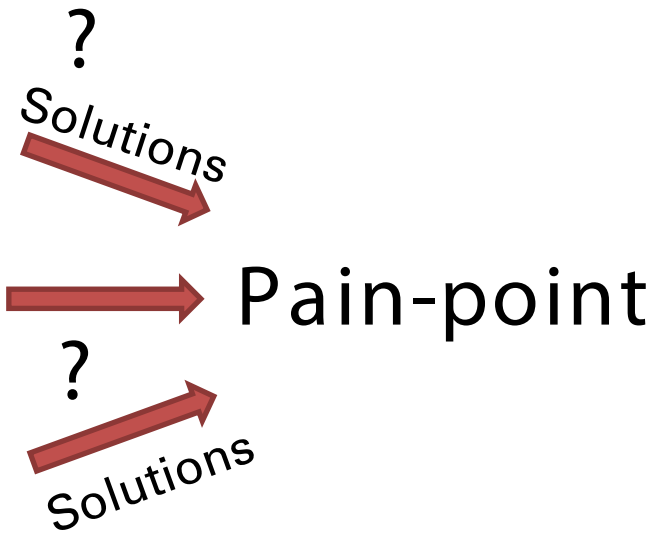
	North America Market Size (BSF)	Performance Based Competition	Low Cost Competition
Laminated Veneer Lumber (LVL)	1.2	MF (Cost Basis: $0.55/lb.)	PF (Cost Basis: $0.25/lb.)
Plywood	4.5	pMDI (?) (Cost Basis: $0.70/lb.)	UF/PF (Cost Basis: $0.25 to 0.41/lb.)
Oriented Strand Board (OSB)	16.3	pMDI (Cost Basis: $0.70/ lb.)	UF/PF (Cost Basis: $0.25 to 0.41/lb.)
PAG Cost Basis:		$0.37 to 0.40/lb.	

CARB/EPA Rule change





- New limits on formaldehyde emissions
- Need for an alternative
  - Could this be PAG?



CARB standards → New EPA Rules

2009
CARB Phase 1, formaldehyde emissions capped at 0.08 ppm

2010
CARB Phase 2, compliant. These emissions capped at 0.05 ppm as well as household and other finished goods containing these products.

2011
Formaldehyde added to federal government's carcinogen list

March 22, 2019
Composite wood products must be labeled as TSCA Title VI compliant. These products include: hardwood plywood (0.05 ppm), medium density fiberboard (0.11-0.13 ppm), and particleboard (0.09 ppm).

December 12, 2016, EPA published in the Federal Register a final rule to reduce exposure to formaldehyde emissions from **certain wood products produced domestically or imported** into the United States.

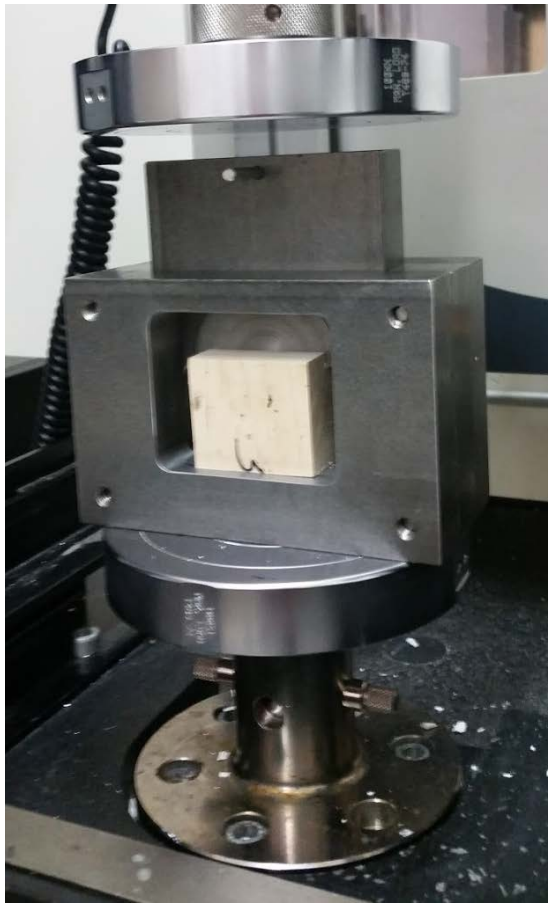
June 1, 2018
Composite wood products **sold, supplied, offered for sale, manufactured, or imported** in the United States are required to be labeled as CARB ATCM Phase II or TSCA Title VI compliant.

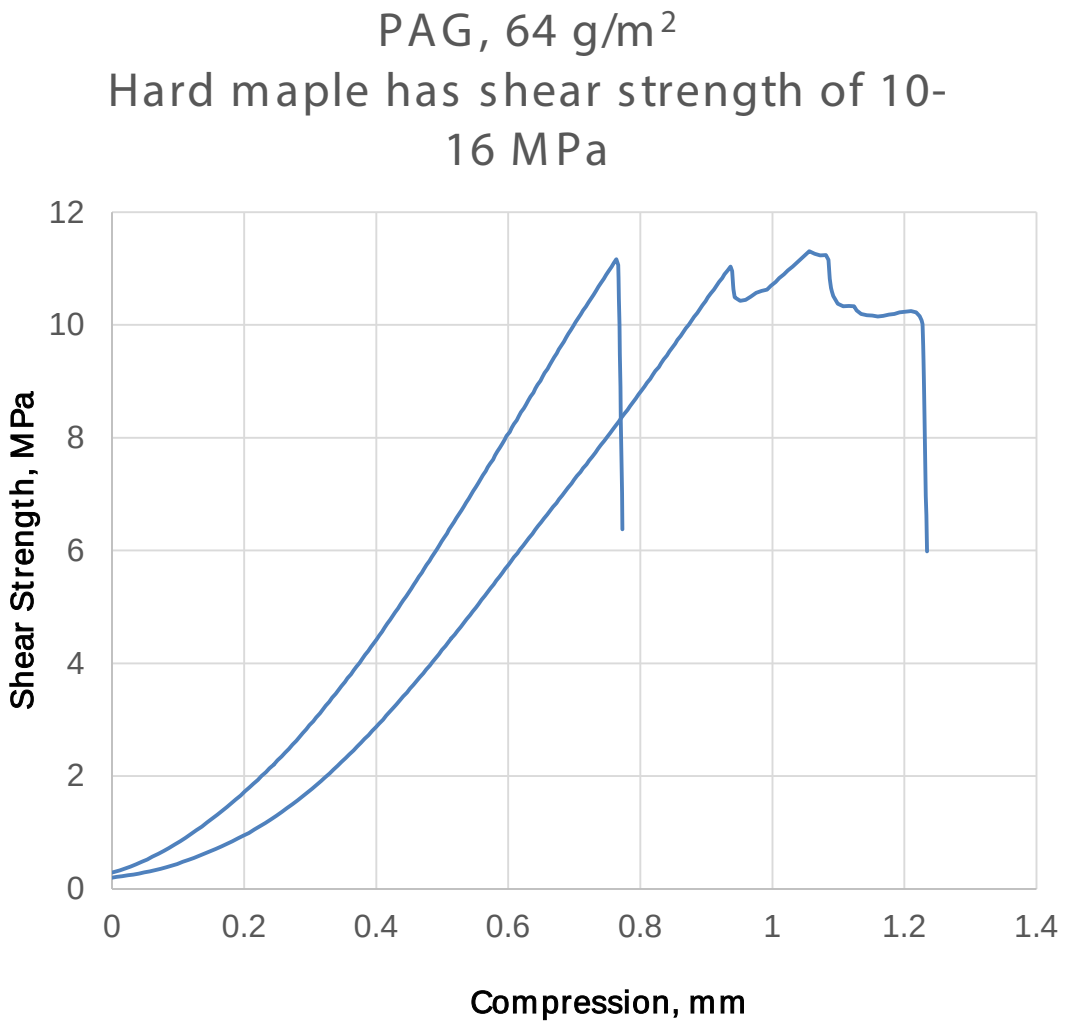
PAG advantages

- Water soluble – VOC free
- Strong physical interaction with cellulose surfaces
- Sticky // "Green tack"
- Curable through residual acrylic functionality
- Formaldehyde free
- Cost-advantaged to pMDI or MF

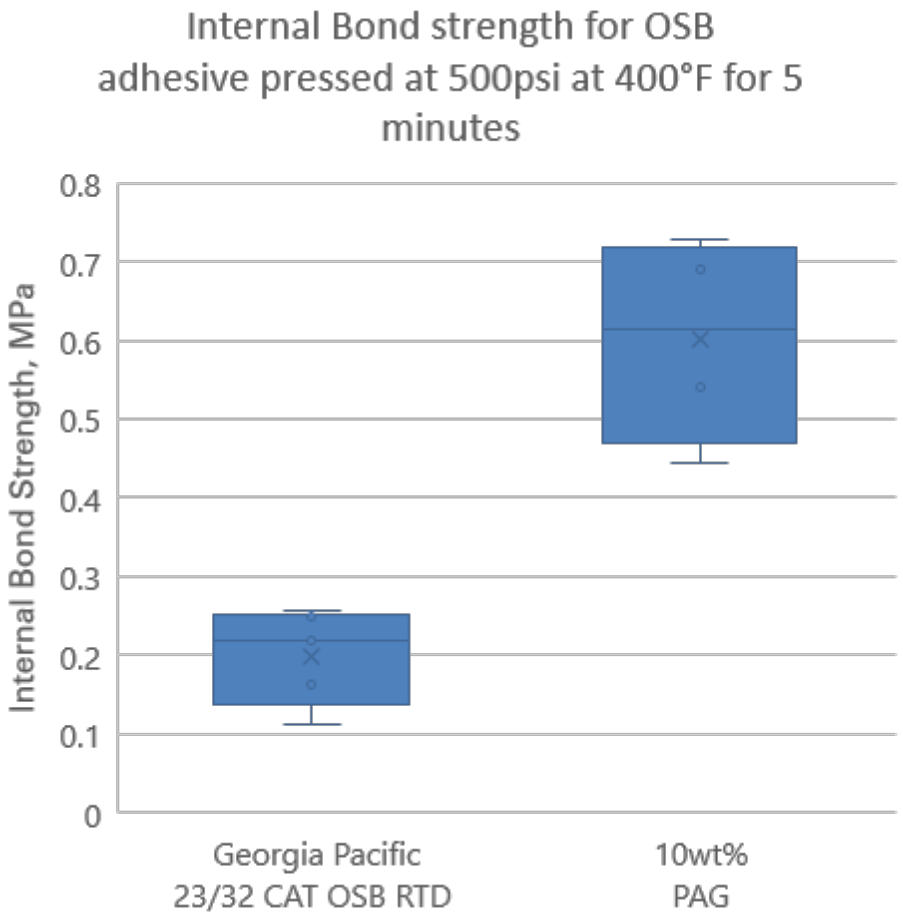


Is it strong enough?
ASTM D-905 hard maple shear tests





Is it strong enough?
OSB performance



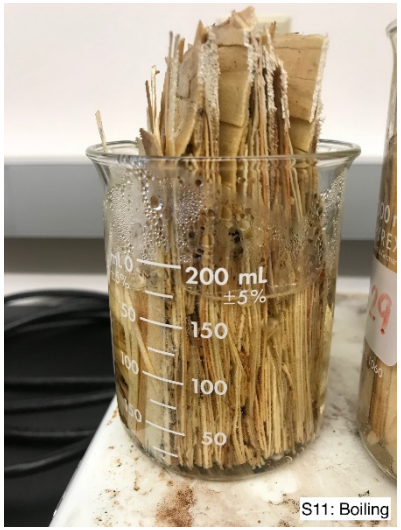


Does it resist water?

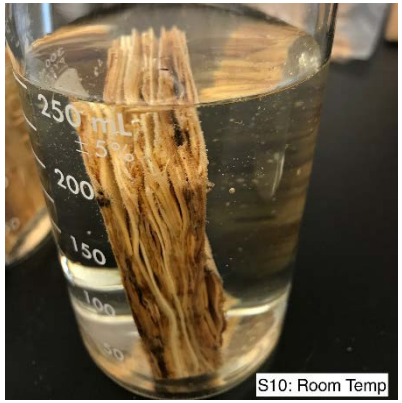
Not so much…



10% PAG after 60 minutes room temp water



10% PAG after 10 minutes in boiling water





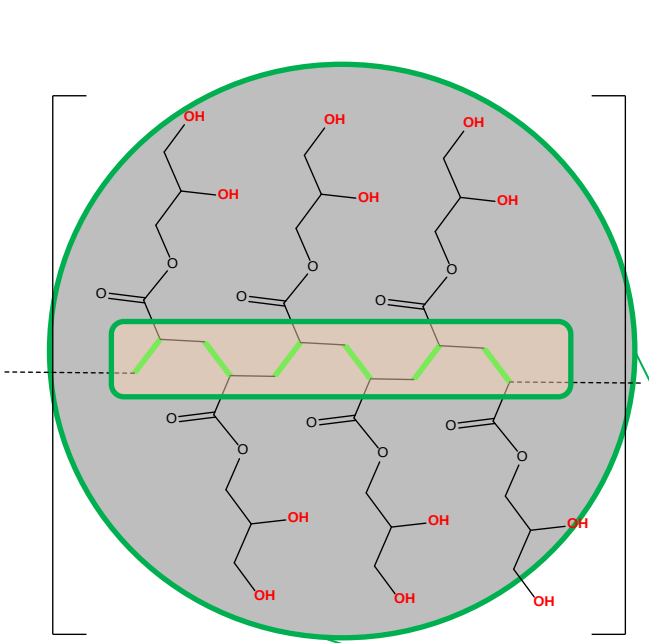
15% PAG after 60 minutes in room temp water

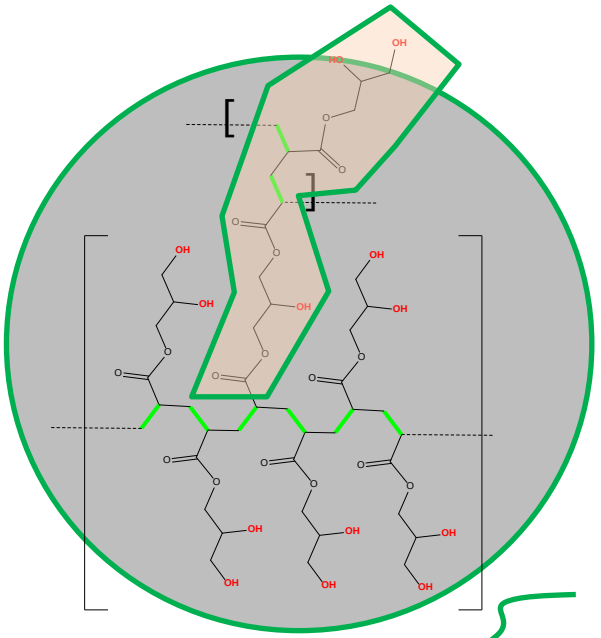


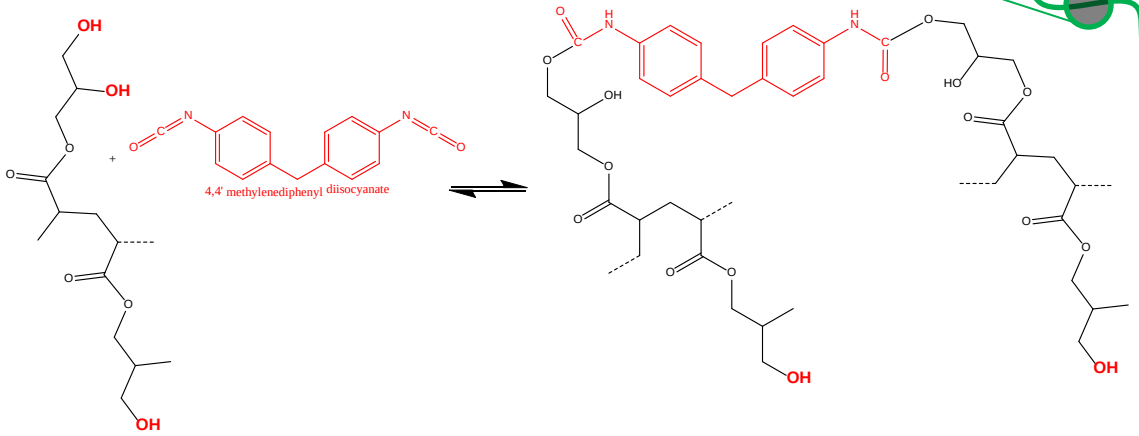
15% PAG after 10 minutes in boiling water

Does it resist water?

But...







Plywood test samples

Hot pressed 5 minutes at 0.7- 2 MPa at 150-250°C

Cut into ASTM D906 shear samples 81 mm x 25 mm



Tested in load frame according to *PS1-95 Construction and Industrial Plywood*:

- Dry
- Soaked 30 minutes under 85kPa psi vacuum, soaked 4 more hours, tested wet
- Boiled 4 hours dried at 65°C for 15 hours, boiled 4 more hours, tested wet

Plywood Water Resistance

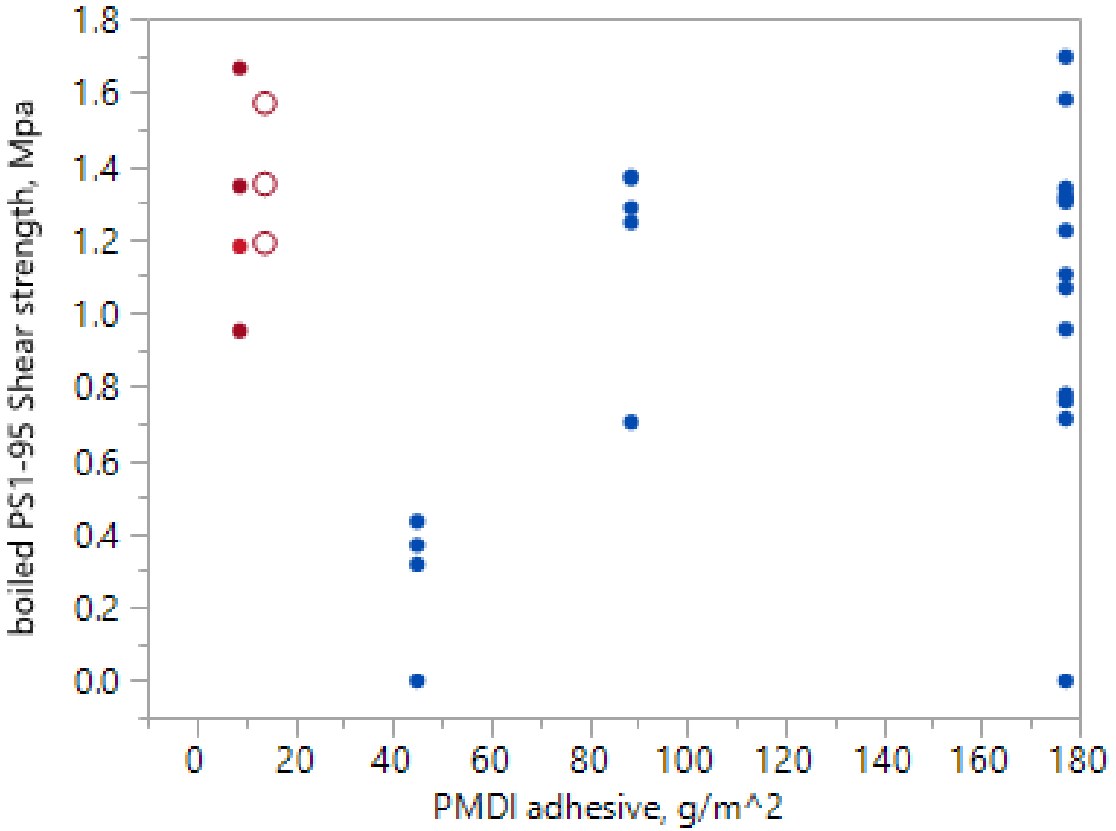
Why PAG?

- Equal performance with less adhesive

PMDI is currently used at application rates of 50-100 g/m^2

9-14 g/m^2 PMDI with 45-48 g/m^2 PAG ≥ 50-180 g/m^2 PMDI

Boiled 4 hours, dried at 65°C for 15 hours, Boiled 4 more hours, tested wet



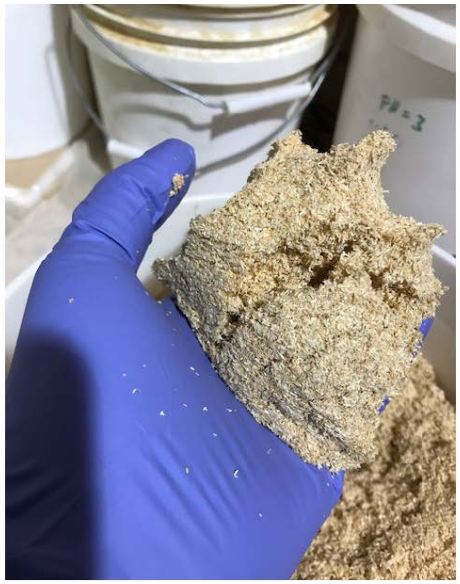
Particle Board

Why PAG?

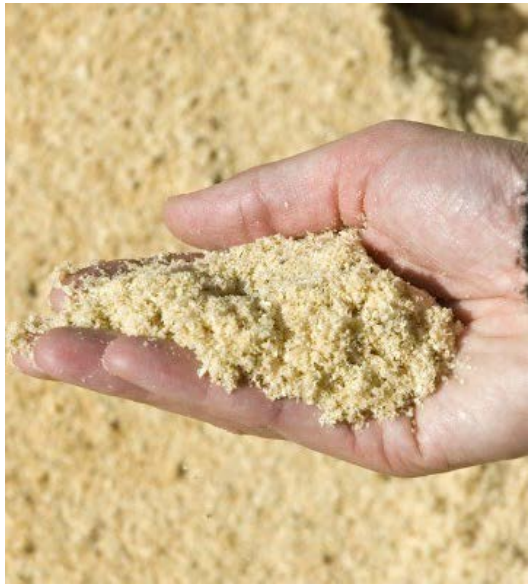
- Offers exceptional green tack, unlike pMDI



6wt % PAG



4 wt% PAG



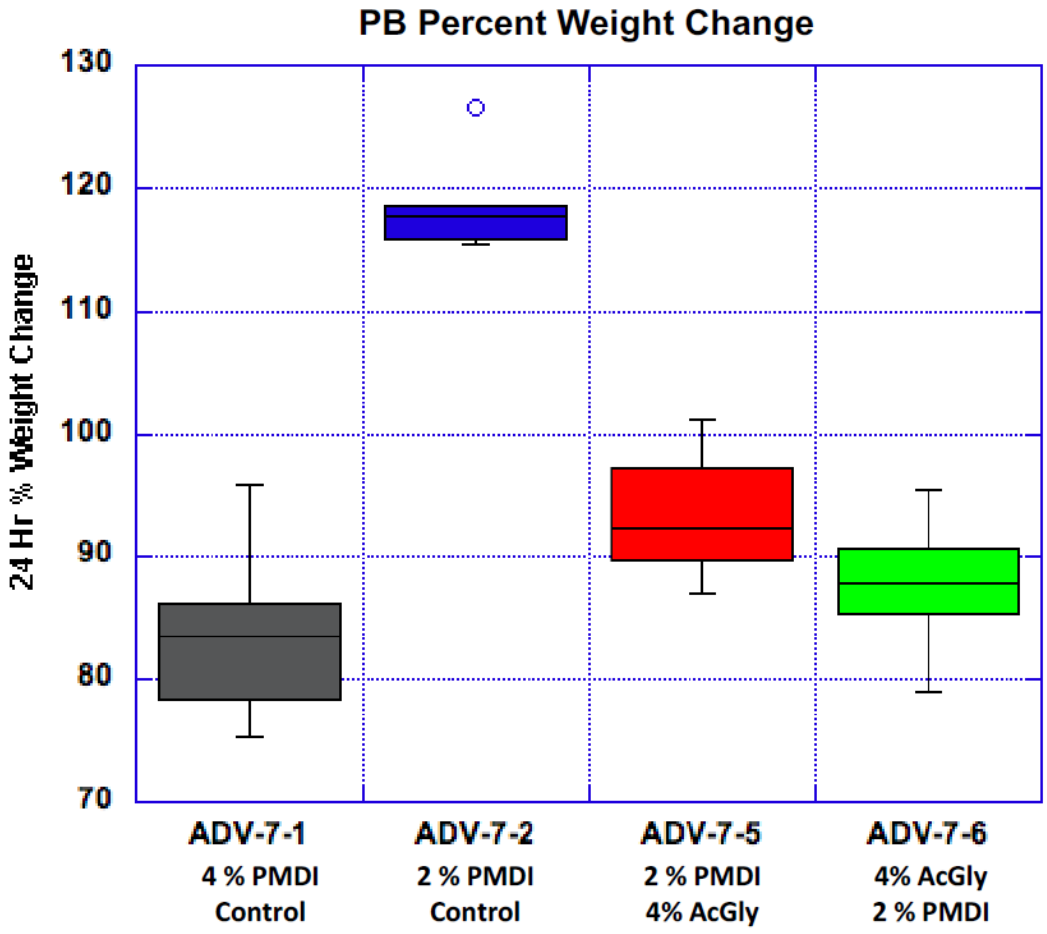
4 wt % PMDI

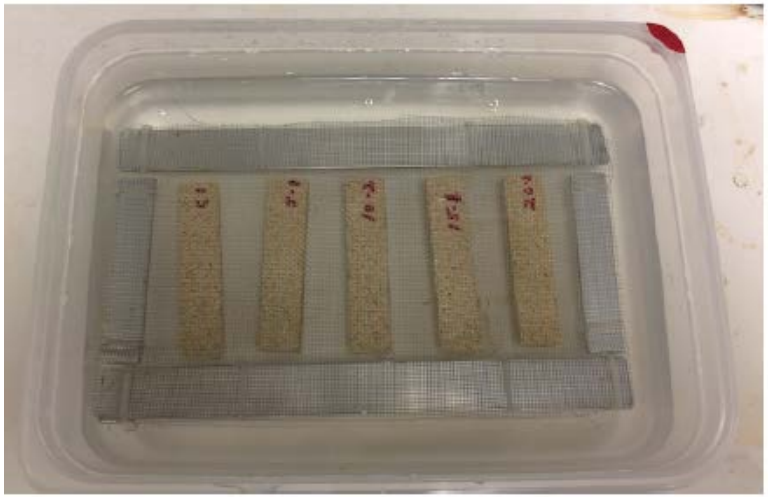
"Snowball" test

Particle Board

Why PAG?

- Can reduce costly pMDI by 80% and retain water resistance

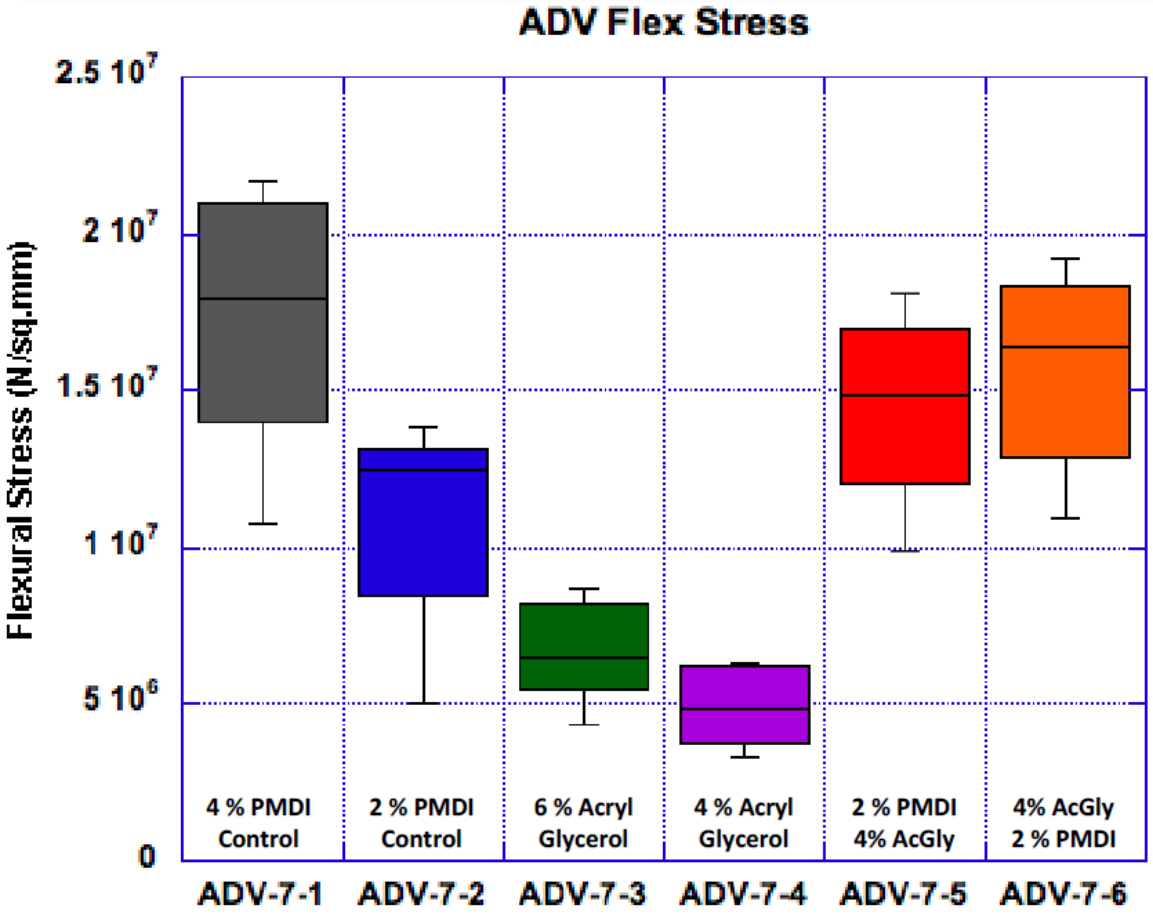




Particle Board

Why PAG?

- Can reduce costly pMDI by 80% and retain strength





Medium Density Fiberboard

Why PAG?

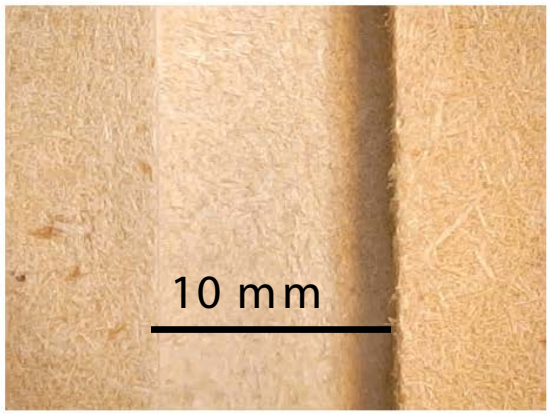
- Improved machinability



2 % PMDI Control



4 % PMDI Control



4 % Adv. / 2 % PMDI

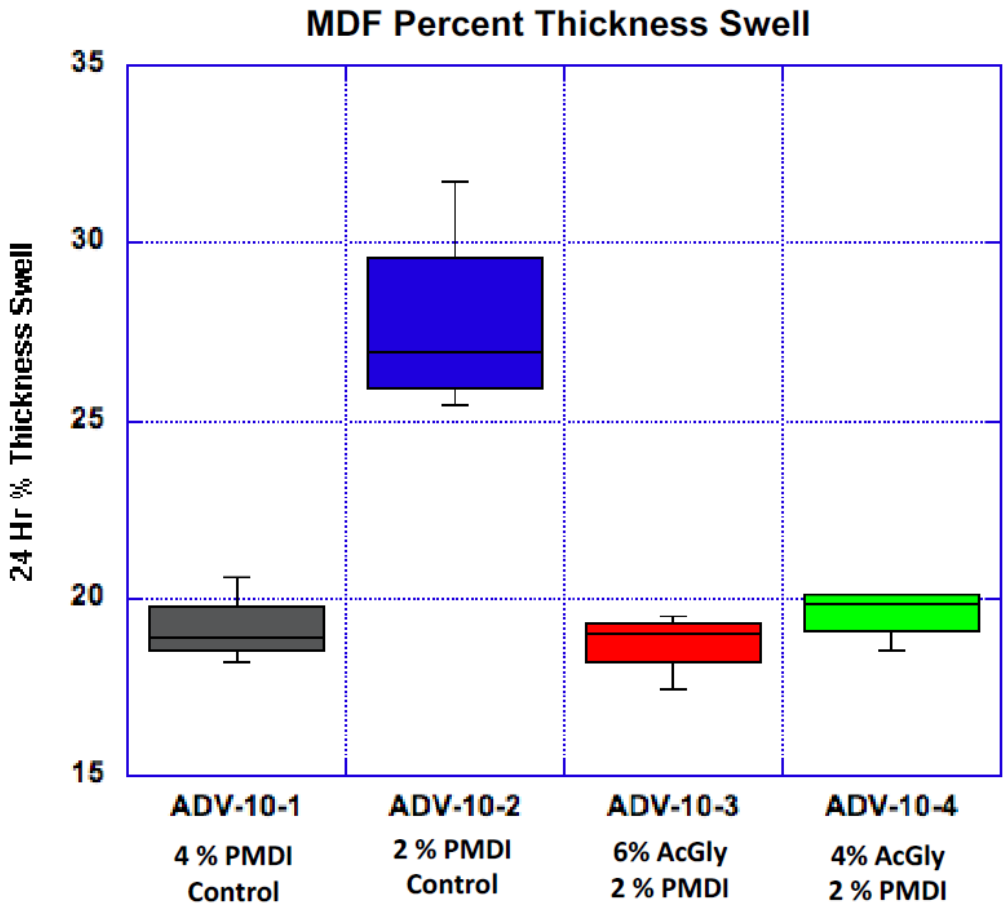


6 % Adv. / 4 % PMDI

Medium Density Fiberboard

Why PAG?

- Can reduce costly pMDI by 80% and retain water resistance





Future Plans

- Piloting trials at Fraunhofer institute for wood research
- 3000 lbs PAG adhesive for full-scale production trial

AGC
ARGO GENESIS CHEMICAL LLC





62/668,655: Thermoplastic Poly Acrylated Glycerol Adhesives Useful in Cellulosic Products

Thanks to…

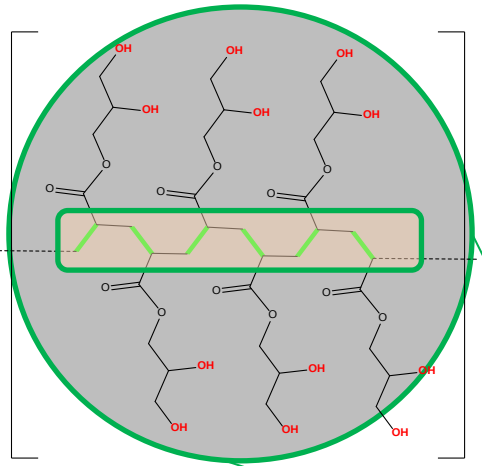
- USDA
- Adventus
- Joe Marcinko at Polymer Synergies
- Argo Genesis Chemical LLC
- Seneca Petroleum
- Cochran research group

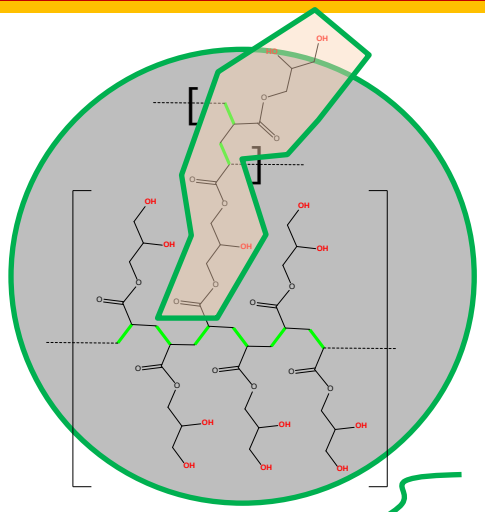


And to you all at ISBBB 2018!

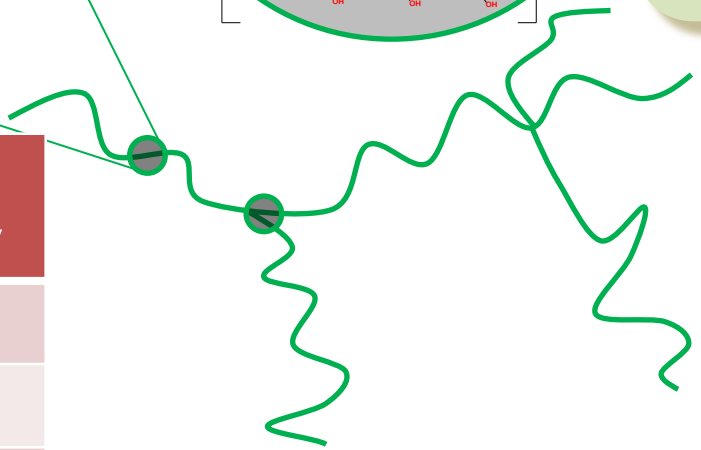
PAG — Poly(acrylated glycerol)

Linear chain segments from monoacrylated glycerol monomeric unit.





Branch points can occur from any monomeric unit having a degree of acrylation greater than 1, e.g., di-acrylated glycerol.



C=C	M_n, kDa	PDI	Water Solubility
1.2	192	3.1	<5%
1.2	528	2.4	20%
1.2	882	1.95	30%
1.6	200	2.76	<5%
1.6	645	2.47	<5%
2.0	194	2.85	<5%

-OH group is inert in acrylic polymerization reactions, irrespective of chemical mechanism